CEREAL CHEMISTRY

Vol. VI March, 1929 No. 2

CORRELATION STUDIES WITH DIVERSE STRAINS OF SPRING AND WINTER WHEATS, WITH PARTICULAR REFERENCE TO INHERITANCE OF QUALITY[1]

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(Received for publication, November 24, 1928)

One of the greatest difficulties in breeding improved varieties of wheat is the lack of a reliable method of estimating milling and baking quality when only small quantities of seed are available. Several pounds of seed are needed for preliminary milling and baking trials, and such quantities of seed cannot be obtained from the small progenies grown from the seed of a single parent plant—the usual method of growing the progenies during the segregating generations. If the plant breeder crosses two or more varieties to obtain certain desirable combinations of characters, several years must elapse before homozygous lines containing the desired sorts can be obtained. A reliable index of quality, when only small amounts of seed are available, would be of great value.

The purpose of this paper is to give the results of milling and baking trials of strains of wheat that have been obtained for the most part from purified hybrids selected from crosses. The extent to which milling and baking qualities are inherited from year to year was studied by the use of inter-annual correlation coefficients, and the importance of certain characters, particularly crude protein content and grain texture, in relation to loaf volume was given special attention.

[1] Published with the approval of the Director as Paper No. 819, Journal Series, Minnesota Agricultural Experiment Station.

Previous Studies

Zinn (1920), of the Maine Experiment Station, studied 40 pure lines of wheat during 1917 and 1918. The extent to which crude protein content was inherited, i.e., as a strain characteristic, was expressed by an inter-annual correlation coefficient of $+0.381 \pm 0.092$. He stated that there was a direct relation between protein content and loaf volume when the pure lines from a single variety were considered. The suggestion was made that quantity of protein as determined by analysis and quality of gluten as indicated by the chewing test might aid the plant breeder in making his selections. Later, Zinn (1923) made an extensive biometrical study of published data of chemical, milling, and baking tests of American wheats and found, for the most part, positive and significant correlations between protein content and loaf volume. In pure lines the correlation coefficients ranged from $+0.4621 \pm 0.0766$ to $+0.5548 \pm 0.0934$. These studies, however, did not differentiate between environmental and hereditary factors and consequently are not directly applicable to the work of the plant breeder where the varieties are grown in direct comparison with each other.

Extensive studies have been made of the correlation between crude protein content and loaf volume. Mangels (1926) studied samples of hard spring wheat grown in North Dakota for eleven crop seasons. He obtained correlation coefficients ranging from -0.014 to $+0.547$, of which two were negative and nine were positive coefficients. All positive correlation coefficients were significant in the light of their probable errors. Bailey and Sherwood (1926) studied samples of wheat grown in Minnesota, Montana, North Dakota, and South Dakota during five seasons and obtained a correlation between protein content and loaf volume of $+0.271 \pm 0.038$ altho the relationship was not linear. Grewe and Bailey (1927), from seventeen flours collected from various parts of the United States and Canada, found a correlation between protein content and loaf volume of $+0.678 \pm 0.091$. Blish and Sandstedt (1925) studied the relation in Nebraska wheats of loaf volume and protein content and obtained a correlation coefficient of $+0.304 \pm 0.058$. Coleman and others (1927), with hard red spring and hard red winter wheats grown in 1923 and in 1924, obtained three positive correlation coefficients for loaf volume and protein content of between $+0.4$ and 0.5. With winter wheat for 1924, a negative value of -0.0370 ± 0.0773 was obtained, altho

they stated that there was a positive relation for protein content and loaf volume for samples containing up to 12% protein.

The studies mentioned are representative and indicate that, in general, there is a significant and positive relation between protein content and loaf volume of samples grown under varying environmental conditions. If the correlation was as great in experimental material, i.e., for large numbers of strains grown under comparable conditions, probably the analysis of protein content in hybrid material during the segregating generations would be of value. The results of Montgomery (1913) prove great variability in nitrogen content in small plots of the same pure strain grown in the same field. He stated that single plants should be repeated forty or more times, and rod rows from five to ten times to overcome this variability and obtain a true index of comparative nitrogen content. Clark and others (1926, 1928) correlated the protein content of F_2 plants with that of their F_3 progeny and found no very significant relation. The suggestion has been made recently, however, that determinations of protein content in the segregating generations of wheat crosses and the selection of high protein content lines would aid materially in isolating high quality varieties (Clark, 1928). It appears certain that greater numbers of replications must be made than have been used in the past if such analysis and selections are worth while. It remains to be demonstrated with hybrid material that there is a very significant relation between crude protein content and loaf volume when numerous strains from different crosses are grown under comparable conditions.

Numerous correlation studies have been made of the relation of various seed characters with quality factors as determined by chemical analysis and experimental baking trials. At one time there was a general belief that shriveled wheat with low bushel weight ordinarily contains a higher nitrogen content. An extensive study conducted by Bailey and Hendel (1923) indicates no definite correlation between weight per 1000 kernels and protein content of middlings flour. Schollenberger and Kyle (1927) observed that the protein content of wheat increased with test weight up to 54 pounds per bushel. Above that the protein content decreased as the test weight increased. The "net correlation" between these two variables was —0.2147. Kernel texture was considerably more important than test weight in influencing variation in protein content.

It has been a rather common belief that there was a positive correlation between the percentage of dark, hard, and vitreous kernels and protein content. While recognizing that to some extent such a relation does exist, Frank (1923, a, b) stated that "protein content in hard winter wheat could not be estimated to any degree of accuracy from choosing dark, hard, and vitreous kernels." Mangels and Sanderson (1925), dealing with North Dakota wheat, calculated correlation coefficients between the percentage of dark, hard, vitreous kernels and protein content. The calculated coefficients were as follows

Year	Correlation Coefficient
1922	$+0.660 \pm 0.041$
1923	$+0.067 \pm 0.047$
1924	$+0.453 \pm 0.030$

Shollenberger and Coleman (1926) separated wheat samples into dark, mottled, and starchy groups. Analysis of protein content of the three groups was made separately for the various samples. The dark-kerneled group was decidedly superior and the starchy group decidedly inferior in water absorption, weight of loaf, and crude protein content. Later, Shollenberger and Kyle (1927) studied 1290 samples of hard spring wheat of which 255 were Marquis, 456 were probably Ma··s, and 98 were Kota. They obtained a curvilinear relation b··en protein content and percentage of dark, hard, vitreous kernels, and a correlation coefficient of $+0.5363 \pm 0.0134$ for protein content and kernel texture. Coleman and others (1927) studied the relationship between protein content and percentage of dark, hard, and vitreous kernels in hard red spring and hard red winter wheats of the crops of 1923 and 1924. Correlation coefficients of $+0.6414 \pm 0.0351$ and $+0.3981 \pm 0.0536$ were obtained in the hard spring wheat and $+0.6004 \pm 0.0319$ and $+0.5593 \pm 0.0532$ in the hard red winter wheats in the crop years of 1923 and 1924, respectively. They found the correlation between kernel texture and loaf volume to be of no statistical significance and concluded that kernel texture was of questionable value as an index of baking strength. Newton and others (1927) studied the relation between hardness of kernel, as determined by a machine that measured the pressure required to crack the kernel, and protein content. Within a given sample the vitreous kernels were harder and contained a higher protein content than the starchy kernels. The work of other investiga-

tors that they reviewed, together with their own studies, led them to the conclusion: "It must be concluded that a relation between hardness and protein content exists only within a given sample, in which other factors of difference are ruled out." In a series of samples, however, some evidence of a curved relationship was obtained between the percentage of vitreous kernels and protein content.

Experimental Methods

The spring wheats used in the studies consisted of strains and varieties, mostly of hybrid origin, obtained as a result of co-operative studies between the sections of plant genetics and plant pathology of the Minnesota Agricultural Experiment Station and the Office of Cereal Investigations, of the United States Department of Agriculture. The primary purpose of these investigations is to obtain varieties that are resistant to black stem rust and other diseases and that are as desirable as Marquis in agronomic characters and in milling and baking qualities.

The field tests were conducted at University Farm, Morris, Waseca, and Crookston, Minnesota, in replicated rod-rows. Three-row plots were used, the central row of each plot being harvested for yield comparisons and the border rows for obtaining grain for the milling and baking trials. Three systematically distributed plots were grown at the branch stations and four at University Farm. Each milling and baking sample consisted of a mixture of seed from the four localities. The same relative amounts of seed were used for each locality but in some cases greater amounts of seed were used for one station than for another. This was because of low yields at some stations. The winter wheats studied were grown in rod-row trials at University Farm and Waseca, and each sample consisted of a mixture of seed from the two localities.

The chief characters studied in this problem were loaf volume, percentage of flour, color score and texture score of loaf as determined by the milling and baking test, crude protein percentage in the wheat, and texture of kernel. Texture of kernel was determined by examination of the kernels from each row and by averaging the determinations. The percentage of vitreous kernels and the hardness of kernel was estimated after cutting several transversely, the texture being expressed in percentage, 100 representing entirely hard, vitreous grains. For the spring wheat studies in 1927, stem and leaf rust infection and plumpness of kernel (expressed on a percentage basis) also were studied.

Experimental Results

The data collected were analyzed in two ways. Inter-annual correlation coefficients were calculated for the purpose of learning the extent to which, under the conditions of the experiment, there was a tendency for varieties to react the same way in different seasons. This is a measure of the extent of inheritance under the normal conditions of environment. The extent to which there was an association between the expression of two or more characters was studied also. The inter-annual correlations will be considered first.

Inter-annual correlations.—The data for spring wheat are given in Table I.

TABLE I

INTER-ANNUAL CORRELATION COEFFICIENTS FOR CRUDE PROTEIN IN SPRING WHEAT, LOAF VOLUME, YIELD OF FLOUR, COLOR SCORE, TEXTURE SCORE OF LOAF, AND TEXTURE OF KERNEL

	N = 26	N = 23	N = 34
$Protein_{45}$	$= +0.42 \pm 0.11$	$P_{46} = +0.25 \pm 0.13$	$P_{56} = +0.42 \pm 0.10$
$Loaf\ volume_{45}$	$= +0.13 \pm 0.13$	$L_{46} = +0.29 \pm 0.13$	$L_{56} = +0.36 \pm 0.10$
$Yield\ of\ flour_{45}$	$= +0.36 \pm 0.12$	$F_{46} = -0.01 \pm 0.14$	$F_{56} = +0.13 \pm 0.11$
$Color\ score_{45}$	$= +0.27 \pm 0.12$	$C_{46} = +0.09 \pm 0.14$	$C_{56} = +0.33 \pm 0.10$
$Texture\ score,\ loaf_{45}$	$= +0.28 \pm 0.12$	$T_{46} = +0.16 \pm 0.14$	$T_{56} = +0.32 \pm 0.10$
$Texture,\ kernel_{45}$	$= +0.63 \pm 0.08$	$S_{46} = -0.12 \pm 0.14$	$S_{56} = +0.65 \pm 0.07$

The subscripts, $protein_{45}$ etc., refer to the seasons 1924 and 1925 respectively. The symbols N = 26, N = 23, etc., refer to the number of comparisons (varieties or strains) correlated. In general, the correlations between 1924 and 1925 and between 1925 and 1926 were of similar magnitude. Those between 1924 and 1926 were much smaller and, in the light of their probable errors, which were large, of little mathematical significance. It is apparent that environmental conditions in 1924 and 1926 were very different.

The inter-annual correlation coefficients for crude protein content were all positive, being respectively $+ 0.42 \pm 0.11$, $+ 0.25 \pm 0.13$ and $+ 0.42 \pm 0.10$.

Loaf volume, under the conditions of the experiment, gave lower inter-annual correlations than protein content. The inter-annual correlation for flour percentage between 1924 and 1926 was of negative value and very small. It was positive in the other two comparisons, being very low in comparing 1925 with 1926 and about three times its probable error in 1924 and 1925. Inter-annual correlation coefficients for both color score and texture score of loaf were positive and of similar magnitude. This indicates a slight tendency for varieties to react the same way in different seasons. For texture of kernel, the inter-annual correlation coefficients for 1924 with 1925 and for 1925

with 1926 were over +0.6 while the correlation between 1924 and 1926 was negative and low. These data indicate the extent to which normal seasonal conditions modify the expression of characters, and prove rather conclusively the necessity for continuing studies of this nature over several crop seasons.

Eighteen varieties and hybrids of winter wheat grown in 1925 and 1926 were available for study. The inter-annual correlations for the characters studied are given in Table II.

TABLE II

INTER-ANNUAL CORRELATION COEFFICIENTS IN WINTER WHEAT

N = 18	
$Protein_{56}$	$= -0.11 \pm 0.16$
$Loaf\ volume_{56}$	$= +0.26 \pm 0.15$
$Yield\ of\ flour_{56}$	$= +0.42 \pm 0.13$
$Color\ score_{56}$	$= +0.50 \pm 0.12$
$Texture\ score,\ loaf_{56}$	$= +0.46 \pm 0.13$
$Texture,\ kernel_{56}$	$= +0.70 \pm 0.08$

The percentage of crude protein in the grain in 1925 and 1926 was negatively correlated, altho the coefficient was of no statistical significance when judged in the light of its probable error. The inter-annual correlation coefficient for loaf volume was 0.26 ± 0.15, which is of little statistical significance. Coefficients of similar magnitude and between +0.4 and +0.5 were obtained for total flour percentage and for color score and texture score of loaf. Texture of kernel gave an inter-annual correlation of $+0.70 \pm 0.08$, which indicates that kernel texture was rather strongly inherited and dependent in these seasons upon other factor relationships than those which modify crude protein percentages.

Inter-Relationship of Some Characters

Of most interest were the correlation coefficients for loaf volume and crude protein in the wheat. These data for the spring and winter wheat samples are given in Table III.

TABLE III

CORRELATION BETWEEN LOAF VOLUME AS DETERMINED BY AN EXPERIMENTAL BAKING TRIAL AND CRUDE PROTEIN IN THE WHEAT

Class	No. of samples	Year	Average protein percentage	Correlation coefficient
Spring wheat	26	1924	15.9	$+0.31 \pm 0.12$
" "	34	1925	15.9	$+0.50 \pm 0.09$
" "	34	1926	17.3	$+0.17 \pm 0.11$
" "	24	1927	15.4	$+0.07 \pm 0.14$
Winter wheat	18	1925	12.6	$+0.11 \pm 0.16$
" "	18	1926	16.3	-0.52 ± 0.12

All four coefficients calculated for the spring wheats were positive, altho only two were of any statistical significance. In the case of winter wheat, one correlation was slightly smaller than its probable error and the other was negative and more than four times its probable error. These results were computed from experimental baking trials that were not duplicated in 1924 to 1926. For the spring wheat study in 1927, smaller loaves were baked and each variety was baked four times at least and, in several cases, eight loaves were used. The close agreement between separate bakes indicated that the lack of correlation is not due to variability of experimental procedure. When it is considered, also, that the samples in these studies were obtained from mixtures of seed of replicated trials conducted in four localities for the spring wheat and two for the winter wheat, the conclusion seems obvious that protein determination percentages, under these conditions, are not very valuable as an indication of baking quality as determined from an experimental baking trial.

It would be of interest to determine whether plumpness of grain was correlated with protein content and loaf volume. Notes on plumpness were taken as a regular plan in the breeding material. The seed, however, was recleaned before making up the milling samples and no data were taken on plumpness or shriveling of seed after it was cleaned except in 1927. Calculated coefficients of correlation for protein content and plumpness of grain and for loaf volume and plumpness of grain for 1927 were $+0.22 \pm 0.13$ and -0.27 ± 0.13, which, in the light of their probable errors, are of little statistical significance. A partial correlation coefficient was calculated for loaf volume and protein content in 1927, holding constant kernel texture, stem and leaf rust infection, and percentage plumpness of grain. The calculated coefficient was $+0.04 \pm 0.14$, which is of no statistical significance.

Kernel texture, as determined by the percentage of hard, vitreous kernels, is of importance in grain grading and is generally considered an indication of quality. Correlations between loaf volume and kernel texture, as determined by the method outlined in the experimental procedure for newly produced strains of hybrid origin grown under comparable conditions, are of interest. It will be remembered that kernel texture was rather definitely inherited as indicated by interannual correlation coefficients.

The correlation coefficients were low, three being positive and three negative. Kernel texture and loaf volume had no very significant relationship when different sorts of hybrid origin were studied. Correlation coefficients between kernel texture and protein content were calculated also.

TABLE IV

CORRELATION BETWEEN KERNEL TEXTURE AND LOAF VOLUME

Class	No. of samples	Year	Correlation coefficient
Spring wheat	26	1924	−0.02±0.13
" "	34	1925	+0.30±0.11
" "	34	1926	+0.39±0.10
" "	24	1927	+0.29±0.13
Winter wheat	18	1925	−0.29±0.15
" "	18	1926	−0.04±0.16

These results indicate that with wheats of diverse nature, under the conditions of this experiment, there was no significant correlation between protein content and kernel texture.

TABLE V

CORRELATION BETWEEN KERNEL TEXTURE AND PROTEIN CONTENT

Class	No. of samples	Year	Correlation coefficient
Spring wheat	26	1924	−0.07±0.13
" "	34	1925	+0.26±0.11
" "	34	1926	+0.23±0.11
" "	24	1927	−0.18±0.13
Winter wheat	18	1925	−0.05±0.16
" "	18	1926	−0.19±0.15

All other possible inter-relationships of the characters were studied by the correlation method without establishing any very definite and consistent relationships. Of particular interest were the correlations between factors that were indicative of desirable baking quality. Correlations of loaf volume with color score and texture score of loaf and between color score and texture score of loaf are given in Table VI.

TABLE VI

INTER-RELATIONSHIP BETWEEN LOAF VOLUME, COLOR SCORE, AND TEXTURE SCORE, AS MEASURED BY CORRELATION COEFFICIENTS

Class	Year	No. of samples	Loaf volume and texture score of loaf	Loaf volume and color score of loaf	Color score and texture score of loaf
Spring wheat	1924	26	+0.07±0.13	+0.23±0.13	+0.47±0.10
" "	1925	34	+0.28±0.11	+0.48±0.09	+0.72±0.06
" "	1926	34	−0.01±0.12	+0.11±0.11	+0.67±0.06
" "	1927	24	+0.40±0.12	+0.13±0.14	−0.29±0.13
Winter wheat	1925	18	+0.35±0.14	+0.40±0.13	+0.04±0.16
" "	1926	18	−0.03±0.16	+0.18±0.15	+0.25±0.15

There was some indication of a slight positive relationship between loaf volume and texture score of loaf as three of the six coefficients calculated were of some significance in relation to their probable errors altho only one of these is more than three times its probable error. The correlations between loaf volume and color score of loaf were all positive, altho not very significant in the light of their probable errors except one, which was over five times its probable error. Five

of the six correlation coefficients for color score and texture score of loaf were positive and one was negative. Three of the positive correlations were mathematically significant, two of these being over +0.6. These results indicate a tendency for a correlation or association of the factors for quality that are expressed as loaf volume, color score, and texture score of loaf.

Discussion

The wheat breeder must produce varieties that excel in milling and baking qualities as well as in agronomic characters and resistance to important pathogenic diseases. Some method of accurately determining milling and baking quality during the early segregating generations, when only small quatities of seed are available, would greatly expedite the breeding program. With no such method available at present, the next best procedure appears to be the comparison of new strains by means of experimental milling and baking trials. The data obtained from such tests were studied by means of correlation coefficients in order to determine the practical value of selecting new strains by means of such simple determinations as kernel texture and protein content. With wheats of diverse nature, kernel texture and protein content were not very significantly correlated with loaf volume as determined by experimental baking trials. Selection of new strains by means of kernel texture is a necessary and desirable procedure in order to obtain new varieties that meet the requirements of grain-grading standards. There is no indication, however, that this selection is valuable as a means of obtaining wheats of high quality as judged by loaf volume determinations. Protein content is generally known to be correlated with loaf volume when commercial samples of wheat are compared. The absence of this relation in wheats of diverse nature indicates that protein content determinations made during the segregating generations are of little value to the wheat breeder as a means of selecting high quality wheat strains.

Because of the importance of the problem and in order to breed new varieties economically, it is necessary that further studies be made with the hope of finding some easily determined physical or chemical character that can be used by the plant breeder as an index of probable quality. It is essential, also, that such quality indices can be cheaply obtained from small samples so that selection for quality can be made before extensive material has been grown.

Summary

1. The data from milling and baking trials of wheats of diverse nature were studied by means of correlation coefficients. The wheat strains were grown in comparative rod-row trials and a mixture of grain from four localities was made for each spring wheat sample and from two localities for each winter wheat sample.
2. Inter-annual correlation coefficients were computed for protein content, loaf volume, flour percentage, color score and texture score of loaf, and kernel texture. There was a general tendency for a correlation between the results of different seasons when wheats of diverse nature were grown under comparable conditions. Three of four correlations for protein content were positive with two about four times their probable errors. The four inter-annual correlations for loaf volume were positive, altho only one was more than three times its probable error. For flour percentage, three of the four correlation coefficients were positive, and two were more than three times their probable errors. The correlation coefficients for color score and texture score of loaf gave results of a similar nature, and all calculated inter-annual correlation coefficients were positive with two correlation coefficients three and four times their probable errors respectively and the other two not very significant statistically. Three of the four inter-annual correlations for kernel texture were positive and one was negative. The three positive coefficients were over $+0.6$.
3. Neither protein content nor kernel texture was significantly and consistently related to loaf volume as determined by calculated correlation coefficients.
4. With wheats of diverse nature, there was no indication of a significant positive relation between protein content and kernel texture.
5. There was some indication of a slight general tendency for a positive relation between loaf volume, color score of loaf, and texture score of loaf altho, for the most part, the extent of association was not very great.

Literature Cited

Bailey, C. H. and Hendel, Julius
1923 Correlation of wheat kernel plumpness and protein content. J. Am. Soc. Agron. **15**:345-350.

Bailey, C. H. and Sherwood, R. C.
1926 Relation of crude protein content of flour to loaf volume. Cereal Chem. **3**:393-401.

Blish, M. J. and Sandstedt, R. M.
1925 Viscosity studies with Nebraska wheat flours. Cereal Chem. **2**:191-201.

Coleman, D. A., Dixon, H. B. and Fellows, H. C.
1927 A comparison of some physical and chemical tests for determining the quality of gluten in wheat and flour. J. Agr. Research **34**:241-264.

Clark, J. Allen and Hooker, John R.
1926 Segregation and correlated inheritance in Marquis and Hard Federation crosses, with factors for yield and quality of spring wheat in Montana. U. S. Dept. Agr. Bull. 1403.

Clark, J. Allen, Florell, Victor H. and Hooker, John R.
1928 Inheritance of awnedness, yield, and quality in crosses between Bobs, Hard Federation, and Propo wheats at Davis, California. U. S. Dept. Agr. Tech. Bull. 39.

Clark, J. A.
1928 Wheat breeding for yield, quality, and disease resistance. Mimeographed Report of First Annual Hard Spring Wheat Conference, pp. 9-27.

Frank, M. L.
1923 Texture vs. protein content vs. kernel weight. J. Am. Assocn. Cereal Chem. **8**:74-82.
1923 Protein content vs. texture vs. kernel weight in southwestern market-run wheat. J. Am. Assocn. Cereal Chem. **8**:165-171.

Grewe, Emily, and Bailey, C. H.
1927 The concentration of glutenin and other proteins in various types of wheat flours. Cereal Chem. **4**:230-247.

Mangels, C. E.
1926 Relation of protein content to baking quality of flour from hard red spring and durum wheats. Cereal Chem. **3**:150-157.

Mangels, C. E. and Sanderson, T.
1925 The correlation of the protein content of hard spring wheat with physical characteristics and baking quality. Cereal Chem. **2**:107-112.

Montgomery, E. G.
1913 Experiments in wheat breeding. U. S. Dept. Agr. Bur. Plant Indust. Bull. 269.

Newton, R., Cook, W. H. and Mallock, J. G.
1927 The hardness of the wheat kernel in relation to protein content. Sci. Agr. **8**:205-219.

Zinn, Jacob.
1920 Wheat investigations. I. Pure lines. Maine Agr. Expt. Sta. Bull. 285.
1923 Correlations between various characters of wheat and flour as determined from published data from chemical, milling, and baking tests of a number of American wheats. J. Agr. Research **23**:529-548.

Shollenberger, J. H. and Coleman, D. A.
1926 Relation of kernel texture to the physical characteristics, milling and baking qualities, and chemical composition of wheat. U. S. Dept. Agr. Bull. 1420.

Shollenberger, J. H. and Kyle, C. F.
1927 Correlation of kernel texture, test weight per bushel, and protein content of hard red spring wheat. J. Agr. Research **35**:1137-1151.

THE RELATION OF HYDROGEN-ION CONCENTRATION AND BUFFER VALUE TO THE BAKING QUALITY OF FLOUR. PART II

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(Received for publication December 31, 1928)

In a previous communication (1929) a study was made of the influence of hydrogen-ion concentration on the baking value of two flours, viz., a fine patent flour of English manufacture made from a mixture of wheats, and a straight run imported Canadian flour made from a blend of graded Manitoba wheats, probably a mixture of No. 1 N. and No. 3 N. Manitoba. The H-ion concentration, or pH value, of the flour was altered by the addition of tartaric acid (up to 8 oz. per sack) at doughing and a wide range of acidity was studied. Thus the pH of the loaves studied varied from 6.12 to 4.86. The conclusion was reached that H-ion concentration was a factor of little importance in bread making and within limits contributed little or nothing to loaf quality. With the patent flour, fermentation was slightly hastened by a greatly increased H-ion concentration of the dough, but this effect was not observed with the straight run flour. The only unmistakable effects that were noticed as directly due to increased acidity were an increased dough toughness and loaf flavor (taste) and these effects were only pronounced with large increases, e.g., a fall of 0.8 in pH. It is common knowledge that acid substances are produced in dough during panary fermentation; after prolonged fermentation the smell of the dough or of the loaf is very "strong" and typically "acidic" in character. The observed ill effects of *prolonged* fermentation on dough and loaf quality cannot be due directly to the small increase in H-ion concentration actually observed. Thus in the work previously recorded the change in pH of the loaf caused by prolonged fermentation (with 2% yeast) of 8 to 11 hours varied from 0.25 to 0.45; such prolonged fermentations completely ruined the doughs for bread making purposes. On the other hand, a change of pH of 2 or 3 times this amount (e.g. 0.7 to 0.9) brought about in the dough at making by means of tartaric acid had an almost negligible, and certainly not significant, effect on loaf quality. Many other chemical and colloid changes, besides acid production, take place in a fermenting dough and no doubt each one of them contributes something to the final product. Some of these changes must be of far greater importance as regards their

effects on dough and loaf quality than any small, or even considerable, change of H-ion concentration is likely to be.

This work appeared to militate against the widely accepted conclusions of Jessen-Hansen (1910), according to which loaf quality improves with increasing acidity up to a H-ion concentration equivalent to a pH of about 5.0, above which loaf quality deteriorates. Our work suggested that no alteration in loaf quality occurs as a result of changing H-ion concentration over a wide range—a range wide enough to include any variations likely to be met with in commercial flours or due to commercial practices such as treatment with chlorine or beta-gas.[1] If acidity is raised (e.g. pH to well below 5.0) or lowered (e.g. to pH greater than 7.5) sufficiently, serious damage to dough and loaf quality must result; but it is desired to emphasize the fact that our experiments have demonstrated that the drastic deterioration of dough and loaf brought about by prolonged fermentation is not due to alteration of H-ion concentration but to some other factor or factors.

Our earlier work was conclusive for only two flours. In view of the scientific interest and importance of the point, it was desirable that the work should be extended to cover a wide range of flours. This has been done and the present report deals with results obtained with the following flours and flour blends: English, blends of English and Russian, and of English and Manitoba, Plate, Karachi, a commercial bakers' grade or clear flour (called Fines), and a very low grade flour (J-roll and collected offal flour). Further experiments have also been carried out with the fine patent flour (Millennium) dealt with in the former paper and with a commercial straight run flour ("CCC"). All were commercially milled flours and were free from chemical improvers.

Effect of Hydrogen-Ion Concentration on Gas Production in Doughs

The quantity of gas produced by a dough under commercial baking conditions is a matter of the greatest importance in the English milling industry. Flours are normally made from mixtures of wheats of widely different strengths and gassing qualities. Wheats as diverse as Manitoba, Indian, Durum, Plate, and English may be used together or in succession in the same mill and from such diverse material the English miller has to produce a flour of regular quality—regular in strength and regular and adequate in gas production. A flour that produces insufficient gas, especially during the critical or proving period of fermentation, will be called "weak" by the baker although the same

[1] It was pointed out in the previous paper (Fisher and Halton, 1928) that the striking improvement brought about in low grade flours by chlorine treatment may not be and probably is not due to alteration of pH. The very similar improvement effected by Agene is unaccompanied by any appreciable change in pH.

flour might be really a "strong" one and might be so regarded if its gassing power were increased. In other words, so far as the gassing power of a flour is under the control of the miller and baker, it should be regarded as a separate problem from strength. We cannot begin to study the strength of a flour until the gassing power has been properly adjusted. This can be done in a variety of ways. This isolation of gassing quality for separate study and its elimination altogether from the problem of strength is perhaps the biggest positive advance that has yet been made in the study of strength. This advance was due to A. E. Humphries, who has emphasized the point of view for many years in the numerous Reports of the Home Grown Wheat Committee of the National Association of British and Irish Millers; it was clearly stated by Humphries in 1911 and again in 1920.

As will be seen in Tables I to VI, gas production is in general not seriously affected by even large increases in H-ion concentration; but poor or inadequate gassers might be more responsive to such variations. In some cases gas production is maintained at a steady rate for slightly longer and in others for somewhat shorter periods at increased acidities. It is possible that some flours just on the verge of inadequacy as gas producers might be improved, as others might be made worse, by increases in H-ion concentration; and some of the improvements recorded by some observers may conceivably be due to improved gassing rather than to increased strength. Certainly few observations of the effect of varying H-ion concentration on gas production in doughs appear to have been recorded. The results given in Tables I to VI show that with a wide range of flours of adequate gassing quality, increase of acidity to well below pH 5 has no significant effect on gas production up to the 4th hour of fermentation (with 2% yeast); beyond this period, rate of gas production may be increased or decreased somewhat or may remain unaffected by increased H-ion concentration.

TABLE I

GAS PRODUCTION OF VARIOUS FLOURS AT DIFFERENT H-ION CONCENTRATIONS

Time	English		50-50 English-Manitoba		Karachi	
	Blank	+Acid	Blank	+Acid	Blank	+Acid
	cc.	cc.	cc.	cc.	cc.	cc.
1st hour	53	55	42	48	31	44
2nd hour	75	76	74	74	65	80
3rd hour	82	84	85	87	100	98
4th hour	95	106	97	103	99	113
5th hour	102	107	101	107	84	84
6th hour	73	74	70	74	53	41
7th hour	44	42	41	40	35	29
8th hour	31	32	30	38	28	15
Total gas in 24 hours	822	873	817	841	690	670
pH of flour	6.20	5.05	6.21	5.30	6.09	5.26
Buffer value	0.79	0.54	0.72	0.63	0.57	0.48

As would be expected from the well known fact that yeast works best in a slightly acid medium, gas production is more sensitive to decreases of H-ion concentration. Up to three hours (with 2% yeast) little falling off in gas production occurs even at acidity as low as pH 7.5. Beyond this period the falling off is more or less rapid and occurs earlier the greater the pH.

The gas production tests were carried out in the way usual in the writers' laboratories. The apparatus employed was essentially that described by Jago (1921) although minor modifications were introduced. The following amounts of material were used for each test: 50 gm. flour, 1 gm. (= 2% of the weight of flour) yeast, 0.625 gm. (=1¼%) salt, and 30 cc. water. The necessary amount of acid or alkali was sieved into the flour or, if a liquid, either added to the liquor or sprayed into the flour. The temperature of fermentation was 80°F.

In the five series of gas tests (the results of which are given in Tables I and II) on English, a 50-50 English-Manitoba blend, choice white Karachi, a commercial bakers' grade or clear flour (Fines), and the very low grade J-roll and collected offal flour, the H-ion concentration of the flour was altered by the careful mixing in of finely powdered tartaric acid at the rate of 6 oz. per sack.

TABLE II
GAS PRODUCTION OF VARIOUS FLOURS AT DIFFERENT H-ION CONCENTRATIONS

Time	Fines		J-roll and collected offal flour	
	Blank	+Acid	Blank	+Acid
	cc.	cc.	cc.	cc.
1st hour	50	60	50	50
2nd hour	85	75	85	85
3rd hour	100	105	90	90
4th hour	115	115	115	125
5th hour	110	130	130	130
6th hour	125	130	130	140
7th hour	120	90	150	160
8th hour	100	65	140	150
Total gas in 24 hours	1295	1230	1795	1860
pH of flour	6.37	5.52	6.49	6.16
Buffer value	0.46	0.67	0.20	0.22

The results for Plate flour are given in Table III. With this flour the effects of both tartaric and phosphoric acids were investigated and the acids were added in two different ways:

(1) They were sprayed into the flour on a commercial scale by means of the Humphries Process.

(2) The tartaric acid was mixed with the flour by sieving and the phosphoric acid was added to the liquor at doughing. No attempt was made to ensure that the same amount of acid was added in each case.

TABLE III

GAS PRODUCTION OF PLATE FLOUR AT DIFFERENT H-ION CONCENTRATIONS

Time	Blank	Tartaric acid		Phosphoric acid	
		Sprayed	Sieved	Sprayed	Added to liquor
	cc.	cc.	cc.	cc.	cc.
1st hour	55	55	50	52	60
2nd hour	85	85	85	88	85
3rd hour	110	125	115	120	120
4th hour	72	60	70	70	60
5th hour	33	37	40	35	45
6th hour	27	28	27	22	25
7th hour	25	24	25	23	25
8th hour	20	18	20	22	20
Total gas in 24 hours	650	658	650	647	660
pH of flour	6.28	5.94	5.50	5.84	...
Buffer value	0.75	0.81	0.67	0.73	...

Gas tests were carried out on another sample of the fine patent flour (Millennium) dealt with in the earlier paper and on two different samples of a commercial straight run flour (called "CCC") made by the same firm. The acid and alkali used were finely powdered tartaric acid and sodium carbonate and were mixed thoroughly into the flour before the addition of liquor. The results are given in Tables IV to VI.

TABLE IV

GAS PRODUCTION OF A COMMERCIAL FINE PATENT FLOUR (MILLENNIUM) AT DIFFERENT H-ION CONCENTRATIONS

Time	Acid pH			Control pH			Alkali pH		
	4.17	4.36	4.64	5.15	5.84	6.54	7.13	7.35	7.51
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
1st hour	65	65	70	75	65	55	50	50	40
2nd hour	100	100	95	90	95	80	80	80	75
3rd hour	120	120	120	120	110	105	95	95	95
4th hour	65	75	70	75	100	85	75	65	65
5th hour	30	40	30	35	40	40	30	33	30
6th hour	20	25	30	25	25	25	15	17	15
7th hour	10	15	20	20	25	25	15	15	15
8th hour	10	15	20	20	20	15	10	10	10
Total gas in 24 hours	505	615	625	635	650	610	570	560	515

The measurements of H-ion concentration were made electrometrically using the quinhydrone electrode as described in the earlier paper.

Baking tests were carried out on the same flour samples on which determinations of gas production had been made.

TABLE V

GAS PRODUCTION OF A COMMERCIAL STRAIGHT RUN FLOUR (CCC) AT DIFFERENT H-ION CONCENTRATIONS, SERIES A

	Acid pH				Control pH	Alkali pH		
Time	4.19	4.41	4.83	5.45	6.19	7.05	7.53	7.80
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
1st hour	65	70	70	60	60	60	50	40
2nd hour	105	100	100	100	95	85	85	75
3rd hour	120	125	130	115	115	110	95	85
4th hour	70	85	90	100	120	90	85	85
5th hour	35	40	40	*	55	40	35	45
6th hour	25	30	30	...	35	25	20	20
7th hour	15	20	30	...	25	20	15	15
8th hour	15	20	20	...	25	15	15	15
Total gas in 24 hours	553	665	711	...	720	654	610	565

*A leak developed in the bottle. This vitiated the remaining determinations of this set.

TABLE VI

GAS PRODUCTION OF A COMMERCIAL STRAIGHT RUN FLOUR (CCC) AT DIFFERENT H-ION CONCENTRATIONS, SERIES B

	Acid pH						Control pH		Alkali pH			
Time	4.14	4.40	4.69	4.92	5.13	5.44	5.69	6.29	6.73	7.14	7.41	7.55
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
1st hour	70	60	55	65	65	60	50	50	50	35	30	9
2nd hour	80	85	85	80	70	80	85	80	80	70	65	41
3rd hour	95	100	105	100	110	95	90	95	90	85	85	80
4th hour	110	110	105	105	110	105	95	95	90	90	80	80
5th hour	105	120	120	125	120	110	110	100	85	75	70	65
6th hour	45	80	80	75	80	90	85	65	50	45	40	50
7th hour	25	45	50	45	50	50	50	45	35	25	30	25
8th hour	15	35	35	40	40	35	35	30	20	20	15	15
Total gas in 24 hours	655	875	970	965	955	940	900	870	830	760	710	605

Baking Tests

For each baking test two dough batches were made up, each of suitable size, using flour, 2% yeast, 1¼% salt, and the correct amount of water at such a temperature as would produce a dough temperature of 80°F. Tartaric acid at the rate of 6 oz. per sack was carefully mixed with one lot of flour before doughing; the second lot contained no added acid. The first loaf from each batch was scaled at 1 hour, after which loaves were scaled at ¾-hour intervals. The temperature of fermentation and proving was 80°F. Tinned 2-pound loaves were made in each case except in the last series discussed under "Straight Run (CCC) Flour, Series B," beginning on page 111. In this series cobs were made.

It was found impracticable to measure loaf volumes and H-ion concentrations of each duplicate series of loaves in one day, so the following procedure was adopted. Each loaf was cut symmetrically and transversely into two halves. All crumb characters were noted;

the contour of the cut surface was drawn on paper and the area enclosed by each contour measured with a planimeter. While these areas are not strictly proportional to the loaf volumes, they are sufficiently so for loaves to be arranged in order of size. After these measurements were made, the H-ion concentrations and buffer values of the crumbs were determined electrometrically.

In the first lot of tests the following flours were studied: English, 50-50 English–No. 1 N. Manitoba blend, 50-50 English–Russian blend, and choice white Karachi. The relevant analytical data for these four flours were as follows:

	English	English-Manitoba	English-Russian	Karachi
Moisture %	16.89	16.50	15.73	14.55
Total nitrogen (N) %	1.48	1.76	1.74	1.39
Protein (N x 5.7) %	8.43	10.05	9.91	7.98
pH (before adding acid)	6.20	6.21	6.13	6.09
pH (after adding acid)	5.05	5.30	5.09	5.26
Buffer value (no acid)	0.79	0.72	0.70	0.57
Buffer value (+ acid)	0.54	0.63	0.52	0.48

English Flour

This was of poor bread-making quality, being more suitable for biscuits.

Doughs.—Both the acid and non-acid doughs required 14 gallons of water per sack. The doughs were very tender, sticky, and difficult to handle. At 3¼ hours they lost their stickiness and were easier to handle. The stability was poor in both sets but the doughs rose well. At 5½ hours they became clay-like and "worked," i.e., rose, sluggishly. They showed poor rise in the oven.

Loaves.—All loaves "thrown" up to 4¾ hours were of good volume for all-English loaves but were of coarse texture with poor spring of crumb. The crumb felt damp to the touch. The acid loaves up to 4¾ hours were of very slightly better crumb color than the untreated loaves and had slightly better crusts; they were also of much larger volume, the difference in volume decreasing from the 1¾-hour to the 4¾-hour loaves. The 5-hour loaves of the two sets were of substantially similar volumes. In other words, the increase in loaf volume, due presumably to increased H-ion concentration, was greater the more unripe the dough. As fermentation proceeded toward ripeness the difference in volume between untreated and treated loaves diminished. As will be shown later, this phenomenon occurs with some other flours but not with all. Jessen-Hansen (1910) in one case recorded an increase of loaf

volume of as much as 36.9%, the other increases recorded varying between 1.6 and 19.8%. Dunlap (1926) states that if the initial H-ion concentration is high enough (e.g., pH 5.9 to 5.7) improved oven spring and consequently increased loaf volume results. Kent-Jones (1927, p. 126) confirmed this with some flours but adds "the addition of acid to the doughing water, so that the pH value is lowered, does not *always* result either in the improvement of the dough or in a good oven spring." In Jessen-Hansen's work the doughs were made with approximately 1.35% yeast (calculated on weight of flour), 0.45% salt, at 77°F., while the proving cabinet was maintained at 86° to 90°F. The length of fermentation appears to have varied between 2 and 2½ hours. It is possible therefore that some of Jessen-Hansen's doughs were under-fermented when placed in the oven. In the light of the observations recorded above, the possibility that under-fermentation may be a factor in the recorded cases of improved oven spring due to increased H-ion concentration ought not to be overlooked.

The H-ion concentrations and areas of cross-section of the loaves are given in Table VII. It will be noticed that in the treated loaves the pH fell only 0.15 in 5½ hours fermentation (i. e. from 1¾ to 7 hours) whereas the untreated dough of much greater pH and smaller buffer action fell 0.39 in the same time. The difference in pH between the two sets varied from 0.88 to 0.64—differences which are relatively enormous—yet the only really significant differences in loaf or dough quality were in the volume of loaves made from unripe doughs.

TABLE VII

H-ION CONCENTRATIONS AND AREAS OF CROSS-SECTION OF ALL-ENGLISH LOAVES

Time to oven	Untreated		6 oz. tartaric acid per sack	
hr.	pH	area (sq. in.)	pH	area (sq. in.)
1¾	5.95	18.6	5.07	25.3
2½	5.85	20.9	5.02	27.2
3¼	5.74	24.0	4.96	29.3
4	5.68	24.7	4.92	29.7
4¾	5.62	26.5	4.92	27.6
5½	5.60	23.7	4.91	23.3
6¼	5.59	21.4	4.92	21.4
7	5.56	21.0	4.92	20.9

50-50 English-Manitoba Blend

Doughs.—Both doughs required 15 gallons of water per sack. The untreated dough was tough and elastic and worked well throughout all stages of fermentation.

The acid dough was not quite so tough as the untreated but was more elastic at first. It was sticky for the first hour, after which the stickiness disappeared and the dough showed a tendency to "bind,"

this tendency becoming more pronounced as length of fermentation increased.

Loaves.—All the loaves were very good up to and including 4¾ hours fermentation, after which volume, color, and spring of crumb deteriorated. The 4-hour loaves were the best. The grain of the loaves was rather open, but the crumb was soft and of good spring. The color and the spring of crumb of the acid loaves were slightly better than those of the untreated loaves.

The H-ion concentrations and areas of cross-section of the loaves are given in Table VIII. The pH of the acid loaves fell by 0.20 and of the untreated loaves 0.26 during 5¼ hours fermentation. The difference in pH of the best loaves (the 4-hour loaves) was 0.73, a large difference in comparison with the trifling differences in other characters. Here again the acid doughs showed a slightly better oven spring than the untreated.

TABLE VIII

H-Ion Concentrations and Areas of Cross-Section of English-Manitoba Loaves

Time to oven hr.	Untreated		6 oz. tartaric acid per sack	
	pH	area (sq. in.)	pH	area (sq. in.)
1¾	6.01	25.0	5.28	27.6
2½	5.97	28.5	5.23	29.8
3¼	5.90	28.3	5.22	28.9
4	5.90	28.2	5.17	29.6
4¾	5.86	27.1	5.14	28.5
5½	5.81	24.3	5.11	23.1
6¼	5.78	22.7	5.09	22.7
7	5.75	21.0	5.09	21.6

50-50 English-Russian Blend

Doughs.—Both doughs required 15½ gallons of water per sack. The untreated dough was of good body and elastic and worked well throughout the fermentation. The treated dough was similar but slightly more elastic and worked rather more freely. Both doughs became soft and sticky after 4 hours and the stickiness increased as fermentation continued.

Loaves.—The H-ion concentrations and areas of cross-section of the loaves are given in Table IX. The loaves were of good color and texture but the crumbs (except that of the best loaves) were moist and doughy and of poor spring. The best loaves were the largest, i.e., those thrown at 4¾ hours. There were no noticeable differences, other than in volume, between the treated and untreated loaves. The earlier treated loaves (i.e., under-fermented), were of considerably larger volume than the corresponding untreated, but of the two best, i.e., fully fermented, loaves the treated was only slightly the larger.

As with the English loaves, the increased oven spring, due apparently to increased acidity, was more pronounced with the under-fermented doughs; the fully fermented did not show this effect.

TABLE IX

H-ION CONCENTRATIONS AND AREAS OF CROSS-SECTION OF ENGLISH-RUSSIAN LOAVES

Time to oven hr.	Untreated		6 oz. tartaric acid per sack	
	pH	area (sq. in.)	pH	area (sq. in.)
1¾	5.90	21.7	5.20	24.6
2½	5.87	21.2	5.16	27.3
3¼	5.88	23.3	5.14	30.7
4	5.80	26.6	5.12	30.1
4¾	5.75	29.2	5.08	30.7
5½	5.73	26.9	5.07	26.2
6¼	5.72	24.6	5.06	24.5
7	5.70	23.9	5.05	22.4

Choice White Karachi Flour

Doughs.—Both doughs required 16¾ gallons of water per sack. The untreated dough was of fair body but claylike and short. It worked very fairly up to 4 hours but after that time became short and sticky. The treated dough was closely similar to the untreated and became similarly sticky and short and difficult to handle after 4 hours fermentation. On the whole it worked, i.e. rose, slightly better than the untreated for the first 4 hours.

Loaves.—All the loaves had peculiar broken crusts, grayish color, and soft silky crumb. The best loaves were thrown at 3¼ hours. There were no noticeable differences between the loaves of the two series.

The H-ion concentrations and areas of cross-section of the loaves are given in Table X. The pH of the acid loaf fell by 0.12 during 5½ hours fermentation—that of the untreated, more lightly buffered loaf fell by 0.21. On the other hand, the difference in pH between the best loaves of the two series was the large amount of 0.66, although these two loaves were closely similar in all characters.

TABLE X

H-ION CONCENTRATION AND AREAS OF CROSS-SECTION OF KARACHI LOAVES

Time to oven hr.	Untreated		6 oz. tartaric acid per sack	
	pH	area (sq. in.)	pH	area (sq. in.)
1¾	5.95	25.1	5.26	24.2
2½	5.90	25.2	5.21	25.9
3¼	5.83	27.3	5.17	26.0
4	5.83	25.4	5.18	23.1
4¾	5.79	21.5	5.16	20.6
5½	5.79	20.2	5.18	19.0
6¼	5.77	20.1	5.16	19.9
7	5.74	19.7	5.14	19.9

A Commercial Bakers' Grade or Clear Flour (Fines)

Doughs.—Both doughs required 15 gallons of water per sack. At 1 hour the untreated dough showed a good rise but with flat top and was beginning to collapse; the acid dough showed an equal rise with a rounded top and was very short. Both doughs worked well up to 4 hours, after which the acid dough worked badly and deteriorated more rapidly than the untreated.

Loaves.—All the untreated loaves were good; the best were thrown at 4 and 4¾ hours. These loaves were similar but the 4-hour loaf was the larger while the 4¾-hour loaf was of better grain. The 5½-hour loaf was good but smaller in volume, of poorer grain, and of tougher, i.e. more corky, crumb.

Of the acid loaves, the best was thrown at 2½ hours. This was smaller than any of the untreated loaves and markedly smaller than the best untreated loaf. It was also definitely inferior in all characters. The other loaves of the acid series were of poor color and open grain. A big fall in loaf quality occurred between the 4- and the 4¾-hour loaves.

The H-ion concentration and areas of cross-section of the loaves are given in Table XI. This flour affords a striking instance of a commercial flour being definitely damaged by an increase of H-ion concentration while at the same time the pH was maintained at a greater value than 5 (in this case 5.3).

TABLE XI

H-Ion Concentrations and Areas of Cross-Section of Loaves from Bakers' Grade Flour

Time to oven hr.	Untreated		6 oz. tartaric acid per sack	
	pH	area (sq. in.)	pH	area (sq. in.)
1¾	6.15	28.4	5.31	27.7
2½	6.06	33.2	5.31	29.9
3¼	5.99	33.8	5.26	30.9
4	5.89	37.2	5.20	31.1
4¾	5.84	24.8	5.18	25.6
5½	5.80	30.9	5.18	25.1

J-Roll and Collected Offal Flour

(This flour would represent the bottom 3 to 5% of an English flour stream.)

Doughs.—Absorption, 16 gallons per sack. Both doughs were claylike and short with no spring. The acid dough was worse than the blank, the surface cracking at 1¾ hours; the untreated dough cracked at 2½ hours.

Loaves.—All were poor, small, and of sodden crumb, muddy color, no spring, and poor texture. There were no observable differences between the two series. The H-ion concentrations and areas of cross-section are given in Table XII.

TABLE XII

H-ION CONCENTRATIONS AND AREAS OF CROSS-SECTION OF THE LOAVES OF J-ROLL AND COLLECTED OFFAL FLOUR

Time to oven hr.	Untreated		6 oz. tartaric acid per sack	
	pH	area (sq. in.)	pH	area (sq. in.)
1¾	6.10	19.4	5.82	20.3
2½	6.04	19.3	5.78	19.3
3¼	6.02	20.8	5.76	20.4
4	5.94	19.6	5.67	20.6

Plate Flour Treated with Tartaric Acid

Loaf Characteristics.—The relevant data are given in Table XIII.

Of the three loaves with 2½ hours fermentation, the untreated was a little smaller than the other two, but in other respects the loaves were closely similar.

TABLE XIII

EFFECT OF TARTARIC ACID ON AREA OF CROSS-SECTION AND H-ION CONCENTRATION OF LOAVES FROM PLATE FLOUR

Time to oven hr.	Blank		Tartaric acid sprayed		Tartaric acid sieved	
	pH	area (sq. in.)	pH	area (sq. in.)	pH	area (sq. in.)
2½	5.93	28.7	5.67	31.6	5.35	31.1
3¼	5.88	24.3	5.68	27.2	5.30	27.9
4	5.86	22.1	5.62	23.7	5.28	23.6
4¾	5.85	23.2	5.54	21.4	5.30	22.8
5½	5.79	22.9	5.55	22.9	5.25	22.6

Of the three thrown at 3¼ hours, the untreated was again the smallest, and the loaf made from the flour into which tartaric acid had been sieved was the largest. The largest loaf also had the best color and the smallest, the poorest. The untreated loaf was somewhat corky in crumb. The best loaves of the series were those thrown at 2½ hours. Those with more than 3¼ hours fermentation were poor and very obviously overfermented.

Plate Flour Treated with Phosphoric Acid

The H-ion concentration and areas of the loaves are given in Table XIV.

Of the loaves with 2½ hours fermentation, that made from the flour sprayed with phosphoric acid was the largest, but in other respects the loaves were similar.

TABLE XIV

EFFECT OF PHOSPHORIC ACID ON H-ION CONCENTRATION AND AREA OF CROSS-SECTION OF LOAVES FROM PLATE FLOUR

Time to oven hr.	Blank		Sprayed with acid		Acid added to liquor	
	pH	area (sq. in.)	pH	area (sq. in.)	pH	area (sq. in.)
2½	5.93	28.7	5.62	31.1	5.72	28.9
3¼	5.88	24.3	5.55	25.9	5.75	32.2
4	5.86	22.1	5.57	23.3	5.64	23.3
4¾	5.85	23.2	5.51	22.7	5.65	23.9
5½	5.79	22.9	5.57	22.8	5.66	23.4

Of the 3¼-hour loaves, the one with phosphoric acid added to the liquor was the largest. This loaf also had the best color and softest crumb, and was equal in quality to the 2½-hour loaves. The other two 3¼-hour loaves were inferior to the corresponding loaves with the shorter fermentation. The 3¼-hour loaf made from the sprayed flour was only slightly better in color and its crumb was only slightly less corky than the 3¼-hour untreated loaf.

All the loaves with a longer fermentation than 3¼ hours were poor.

Millennium (Patent) and CCC (Straight Run) Flours

These two flours were examined over a wide range of H-ion concentration, viz. between pH 4.19 and pH 7.80. Tartaric acid was used to increase the acidity and sodium corbonate to decrease the acidity, or increase the alkalinity. The acid or carbonate was carefully mixed with the flour in the desired proportions by sieving. Single loaves were baked, using our standard short baking system (2% yeast and 3¼ hours fermentation at 80°F.) We had previously ascertained that with these two flours the best loaf was thrown at this time and that the time of fermentation was not significantly affected by alteration in H-ion concentration.

Millennium Flour

The necessary data are given in Table XV.

Doughs.—The absorption was 15 gallons per sack. Doughs 2 to 6 inclusive (i.e., doughs from flours of pH between 7.35 and 5.15) were fairly and equally tough and elastic. Doughs 1 (flour pH = 7.51) and 7 to 9 (flour pH less than 5) were as tough as the others but less elastic, and were short.

At first knock-back (at 1½ hours) doughs 3 to 6 were the best and were similar. Nos. 1 and 2 had risen less and were tougher and shorter than the others. Nos. 7 and 8 rose less than the untreated, had bolder tops, but were tearing. No. 9 showed poor rise, tore badly, and was very "bound."

TABLE XV

H-ION CONCENTRATIONS OF FLOURS AND LOAVES AND AREAS OF CROSS-SECTION OF LOAVES OF A COMMERCIAL FINE PATENT FLOUR (MILLENNIUM)

No.	Flour pH	Loaf pH	pH difference (flour pH—loaf pH)	Loaf area sq. in.
1	7.51	7.38	0.13	24.1
2	7.35	7.08	0.27	22.3
3	7.13	6.53	0.60	23.6
4	6.54	6.02	0.52	24.7
*5	5.84	5.59	0.25	29.2
6	5.15	5.17	—0.02	26.3
7	4.64	4.80	—0.16	23.0
8	4.36	4.53	—0.17	21.6
9	4.17	4.32	—0.15	20.0

*Untreated.

At scaling (2½ hours) doughs 3 to 7 were the best and were similar; they moulded tightly and with good spring. Doughs 1 and 2 were tougher and shorter and moulded with poorer spring. No. 8 was of poor rise, tough, bound, short, and torn. No. 9 was similar to No. 8 but worse.

Loaves.—In the acid series, as the H-ion concentrations increased loaf volume diminished, the crust became paler, the grain closer, the texture coarser, the crumb tougher or more corky, and the color more creamy.

Loaves in the alkaline series were similar but in the reverse order, i.e., loaf quality deteriorated progressively as H-ion concentration decreased.

All the treated loaves were poorer and smaller than the untreated.

Straight Run (CCC) Flour, Series A

The relevant data are given in Table XVI.

Doughs.—The absorption was 15 gallons of water per sack in all. Nos. 3 to 6 (flour pH between 7.05 and 4.83) were equally tough and elastic; No. 2 was slightly short, Nos. 1, 7, and 8 were quite short. At scaling (2½ hours), Nos. 3 to 5 stood up best in the boxes, with good round tops; the others showed poor rise and had flat tops, indicating poor stability and poor gas retention. Nos. 3 to 6 moulded tightly with good spring; the others were claylike and short. Nos. 3 to 5 worked well in final proof; No. 6 was slightly inferior; the others were poor.

Loaves.—Loaves 4 and 5 were closely similar, No. 5 being of slightly better color and bloom; No. 6 was also better in color but of tougher crumb; Nos. 7 and 8 were quite tough of crumb. Loaves 1 to 3 were all tougher in crumb than the untreated; 2 and 3 were creamier in color, No. 1 was quite yellow. The grain was close and even in all. On the whole, No. 5 was slightly the best loaf of the series.

TABLE XVI

H-Ion Concentrations of Flours and Loaves and Areas of Cross-Section of Loaves of a Commercial Straight Run Flour (CCC)

No.	Flour pH	Loaf pH	pH difference (flour pH—loaf pH)	Loaf area (sq. in.)
1	7.80	7.62	0.18	24.4
2	7.53	7.31	0.22	27.0
3	7.05	6.50	0.55	28.1
*4	6.19	5.77	0.42	28.8
5	5.45	5.24	0.21	26.4
6	4.83	4.86	−0.03	26.7
7	4.41	4.55	−0.14	22.9
8	4.19	4.34	−0.15	20.4

*Untreated.

This series was re-baked, using a long system (½% yeast and 8 hours fermentation). The loaves were similar to the short system loaves but on the whole the acid treated loaves were larger and better and the alkali treated loaves were smaller and poorer than the corresponding short system loaves.

Straight Run (CCC) Flour, Series B

This was a fresh sample of the same commercial flour used in Series A. Its "natural" H-ion concentration was equivalent to pH 6.12 compared with 6.19 for the previous sample. Twelve loaves were baked over a range of (loaf) pH of 7.55 and 4.14. Cobs, instead of tinned loaves, were made, i.e., at proving the doughs were moulded into balls and allowed to prove side by side on a tray out of contact with each other. The natural "spread" of the dough during proving affords an excellent indication of stability.

The relevant data are given in Table XVII and photographs of the cut loaves are shown in Plate I. Loaf volumes were measured by displacement of rape seed in an apparatus similar to that described by Heon (1922). A technic for this method has been worked out in these laboratories and the apparatus has been calibrated against wooden loaves of known volumes. Triplicate determinations are carried out on each loaf. With elaborate precautions to obtain reproducibility of results the margin of error is large but does not exceed 3%.

Doughs.—The absorption was 15 gallons of water per sack in all. Nos. 6 (the untreated) and 7 were fairly tough, i.e., of good "body," and elastic and closely similar.

Nos. 8 and 9 were tougher and short, both characters being more pronounced in No. 9 than in No. 8.

No. 10 was very tough and short.

Nos. 11 and 12 were still tougher and handled claylike with poor spring.

TABLE XVII

H-ION CONCENTRATIONS OF FLOURS AND LOAVES (COBS) AND LOAF VOLUMES OF STRAIGHT RUN FLOUR (CCC) OF VARYING H-ION CONCENTRATION

No.	Flour pH	Loaf pH	pH difference (flour pH—loaf pH)	Loaf volume cc.
1	7.98	7.55	0.43	2637
2	7.53	7.41	0.12	2815
3	7.29	7.14	0.15	2912
4	7.07	6.73	0.34	3198
5	6.64	6.29	0.35	3155
*6	6.12	5.69	0.43	3365
7	5.65	5.44	0.21	3185
8	5.19	5.13	0.06	3080
9	4.86	4.92	—0.06	3046
10	4.59	4.69	—0.10	2846
11	4.21	4.40	—0.19	2296
12	4.00	4.14	—0.14	-

*Untreated.

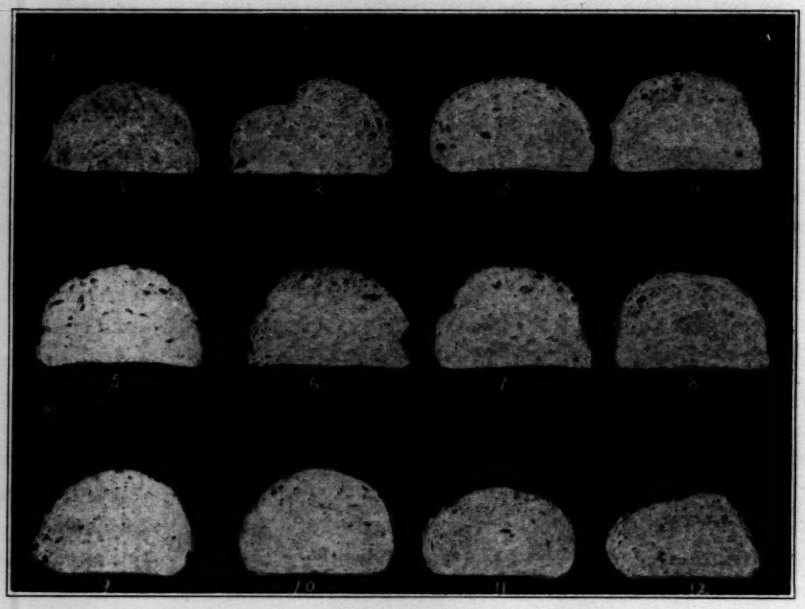

PLATE I

Loaves Made from Straight Run (CCC) Flours of Varying pH

No.	Flour pH	Loaf pH
1	7.98	7.55
2	7.53	7.41
3	7.29	7.14
4	7.07	6.73
5	6.64	6.29
6*	6.12	5.69
7	5.65	5.44
8	5.19	5.13
9	4.86	4.92
10	4.59	4.69
11	4.21	4.40
12	4.00	4.14

*Untreated.

Nos. 5 and 4 were slightly tougher than 6 (the untreated) but were similarly elastic.

Nos. 3, 2, and 1 were very and increasingly tough and claylike. No. 6 rose most rapidly in the boxes in the first and second stages of fermentation; No. 7 rose slightly more slowly than No. 6; Nos. 8, 9, and 10 rose progressively more slowly, and Nos. 11 and 12 rose very little, tearing badly. Doughs 1 to 5 (those with added alkali) worked similarly to one another and more slowly than No. 6; the extent of their rise at first and second knock-back was about half that of No. 6. At molding Nos. 1 to 5 were tougher and more claylike and of poorer spring than 6, the doughs becoming progressively poorer from 5 to 1. No. 7 was closely similar to 6; 8 and 9 were short; 10, 11, and 12 were still shorter, 11 and 12 being thoroughly poor and tearing badly.

Stability.—All the doughs showed good stability on the tray during final proof. Nos. 5, 6, and 7 (pH 6.29 to 5.44) were closely similar. Nos. 1 to 4 appeared slightly less bulky than 8; 9 and 10 slightly more bulky than 5, 6, and 7; 8, 9 and 10 tore slightly during proof. Nos. 11 and 12 were smaller, tore badly, were very tight and tough, and were what a practical baker describes as "bound."

Loaves.—Nos. 3 to 9 showed good oven spring; 10 showed inferior bloom of crust and was torn. Loaves 11 and 12 were of poor volume and crust with no bloom and of dull greyish white color. Nos. 1 and 2 were of good crust color although less bloomy, but were of inferior oven spring.

Loaves 6 to 10 were all good loaves closely similar in crust and general outside appearance and in crumb and grain; No. 6 was slightly softer in crumb than 7 to 10, but the difference was really slight. Crumb color increased slightly in whiteness from 6 to 10; but the color of 11 and 12 was definitely poorer than that of 6. Nos. 5 and 4 were very slightly whiter than 6; 3 was similar to 6; 2 was distinctly yellow and 1 quite yellow. Such other crumb characters as grain, spring, and softness of texture, were closely similar in 6, 5, 4, and 3. Nos. 2 and 1 were definitely poor, being corky of crumb and of poor spring.

The loaf volumes are of some interest. The biggest loaf was the untreated (No. 6), of pH 5.69. This loaf was 5.3% greater than No. 7 of pH 5.44, and 8.3% greater than No. 8 of pH 5.13. No. 6 was also 6% greater than either No. 5 of pH 6.29 or No. 4 of 6.73.

On the whole there was surprisingly little difference in dough or loaf quality between loaves 3 to 10; No. 6, the untreated; was perhaps slightly the best in most characters, very slight progressive deterioration

took place in the direction of both increased acidity and alkalinity, i.e., from loaves 6 to 10 and from loaves 6 to 3.

It should be pointed out that all baking tests recorded in this paper and in others issued from these laboratories were carried out under the writers' close supervision by a highly competent practical baker of long and wide experience in commercial and experimental baking methods. In all cases the baker's written reports are compared with our own notes and observations of the course of fermentation and of dough and loaf characters.

Summary

Extensive baking tests have been carried out with a great variety of flours over wide ranges of H-ion concentration (from pH 7.80 to 4.20) and varying periods of fermentation. The results of the work appear to confirm the conclusion reached in an earlier investigation that H-ion concentration is not a factor of great importance in determining dough or loaf quality. Alterations of H-ion concentration brought about in doughs by additions of acid several times greater than those brought about by prolonged over-fermentation appear to have singularly little effect on dough or loaf characters. Moreover, the effects observed are not always in the same direction, e.g., slight improvement of some characters and slight damage to others may result from increased H-ion concentration.

The effects most commonly but by no means invariably noticed are:

1. Increased dough toughness. Stability appears to be little affected, if at all.
2. More pronounced flavor (taste).
3. Often an improved color of crumb.

Literature Cited

Dunlap, F. L.
1926 The problem of test bakes, with a discussion of certain of their chemical and physical aspects. Cereal Chem. 3: 201-215.

Fisher, E. A. and Halton, P.
1929 Relation of hydrogen-ion concentration and buffer value to the baking quality of flour. Part I. Cereal Chem. 6: 18-33.

Heon, A. A.
1922 A bread measuring device. J. Am. Assocn. Cereal Chem. 7: 152-153.

Home Grown Wheat Committee of the National Association of British and Irish Millers
1920 Chairman's report on the quality of Yeoman wheat. (A. E. Humphries.)

Humphries, A. E.
1911 Some points concerning the treatment of wheaten flour. British Assn., Portsmouth. Pub. in Milling, Sept. 9.

Jago, W. and Jago, W. C.
1921 The technology of breadmaking. Northern Publishing Co., Liverpool, England.
Jessen-Hansen, H.
1911 Etudes sur la farine de froment. I. Influence de la concentration en ions hydrogène sur la valeur boulangère de la farine. Compt.-rend. Trav. Lab. Carlsberg **10:** 170-206.
Kent-Jones, D. W.
1927 Modern cereal chemistry. 2d Ed.

THE PHOSPHORUS OF GRAINS[1]

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(Received for publication, November 6, 1928)

It has been shown that the phosphorus content of wheat, oats, and barley progressively increases as the irrigation water applied increases. The increase in wheat amounted to 55 per cent, in oats to 35 per cent, and in barley to 30 per cent (1923). Taking these figures as a basis, we find the extra phosphorus removed from the soil by a 50-bushel crop of wheat to be 4.9 pounds; by a 100-bushel crop of oats, 2.9 pounds; and by a 75-bushel crop of barley, 4.2 pounds. Consequently the production of irrigated grains removes greater quantities of phosphorus from the soil than does the production of a similar quantity of dry-farm grain; conversely, the user of irrigated grains would be receiving greater quantities of phosphorus than would the user of dry-farm grains. This extra phosphorus may often be of considerable value, for animals kept on a diet consisting principally of irrigated grain would probably find the extra phosphorus sufficient to build strong bones and in other ways increase the nutritive condition of the animal. Whether the value of this increase in phosphorus in the irrigated grains would offset the decrease in protein due to irrigation, remains to be seen. It does indicate, however, that the feeder may often use a calculated mixed ration of the irrigated and non-irrigated grains, depending upon whether more ash or more protein is needed in the diet.

As the phosphorus of grains is in both organic and inorganic forms, the question naturally arises as to whether the increased phosphorus is organic or inorganic. From a consideration of the

[1] From Department of Chemistry, Utah Agricultural Experiment Station. Publication authorized by Director, October 17, 1928.

phosphorus-calcium ratio and the phosphorus-nitrogen ratio it may be concluded that the increase in phosphorus due to irrigation water is primarily inorganic. There is a marked uniformity between the increase in calcium and the increase in phosphorus. Further, the nitrogen decreases whereas the phosphorus increases, making it improbable that there is an increase in the nucleo-proteins or the phospho-proteins in the irrigated grains, consequently the likelihood of the increase of phosphorus being inorganic.

An attempt has been made to throw more light on this subject by making quantitative determinations of the total and inorganic phosphorus in grains grown with varying quantities of irrigation waters.

The total phosphorus was determined volumetrically in the ash according to the official methods of the A.O.A.C. The inorganic phosphorus was determined by the Forbes method (1910). This method is open to criticism, consequently the results must be interpreted with this fact in mind. The results as reported are the averages for several determinations.

TABLE I

TOTAL AND INORGANIC PHOSPHORUS IN WHEAT, OATS, AND BARLEY GROWN WITH VARYING QUANTITIES OF IRRIGATION WATER

Treatment	Wheat			Oats			Barley		
	Total	Inorganic	Percentage inorganic	Total	Inorganic	Percentage inorganic	Total	Inorganic	Percentage inorganic
	%	%		%	%		%	%	
No irrigation water	0.295	0.0186	6.3	0.279	0.0337	12.1	0.309	0.0232	7.5
15 inches " "	.323	.0192	5.9	....	.....	.....	....	.....	.....
20 " " "	....	.....	.....	.340	.044	12.9	.335	.0211	6.3
35 " " "	.458	.026	5.7	0.378	0.033	8.7	.402	.0376	9.4
52½ " " "	....	.....	.....	....	.....	.....	0.375	0.0314	8.4
67½ " " "	0.424	0.021	5.0	....	.....	.....	....	.....	.....

The wheat showed an increase in total phosphorus as the irrigation water applied increased up to 35 inches; 67.5 inches of irrigation water caused a decrease. Altho there is an increase in the inorganic phosphorus as shown by the Forbes method, the main increase is organic phosphorus. Between 5% and 6.3% of the total phosphorus of wheat is inorganic.

The oats increased in phosphorus as the irrigation water applied increased. Practically all the increase, according to these results, is in the form of organic phosphorus. More of the phosphorus in oats is inorganic than is the case with wheat, an average of 11.2% being in the inorganic form.

There is a marked increase in the total phosphorus of barley due to irrigation water, only a small portion of the increase being

inorganic phosphorus. The inorganic phosphorus varied from 6.3% to 9.4% of the total.

Corn grown on the same farm, with varying quantities of irrigation water, yielded as the average results in Table II indicate.

TABLE II

TOTAL AND INORGANIC PHOSPHORUS IN CORN GROWN WITH VARYING QUANTITIES OF IRRIGATION WATER

Treatment	Total phosphorus	Inorganic phosphorus	Percentage of total phosphorus inorganic
	%	%	
No Irrigation water	0.32	0.040	12.5
5 inches " "	.33	.041	12.4
20 " " "	.33	.050	15.2
30 " " "	.35	.055	15.7
40 " " "	0.33	0.051	15.4

There is only a slight increase in the total phosphorus of corn due to the use of irrigation, but nearly all the increase, according to these results, is in the inorganic form. From 12.2% to 15.6% of the total phosphorus in the corn kernel is in the inorganic form.

The average phosphorus content of corn grown on land with varying quantities of farmyard manure is given in Table III.

TABLE III

TOTAL AND INORGANIC PHOSPHORUS IN CORN GROWN ON SOIL RECEIVING VARYING QUANTITIES OF MANURE

Treatment	Total phosphorus	Inorganic phosphorus	Percentage of total phosphorus inorganic
	%	%	
No manure	0.33	0.050	15.1
5 tons manure yearly	.34	.054	15.9
15 " " "	0.33	0.055	16.7

These results point to the conclusion that manure increases the inorganic phosphorus of the corn kernel.

In order to learn the phosphorus content of grains throughout the state, samples were collected from various sections and analyzed. The average results are given in Table IV.

There is a wide variation in the phosphorus content of grains from different sections. The wheat from Richfield contains 2.2 times as much as that grown in Hill Top, the others range between these two extremes. The grain from Richfield has approximately the same phosphorus content as that from Greenville that received 35 inches of irrigation water. The non-irrigated grain from Greenville contains 1.5 times the phosphorus contained in the grain from Hill Top. It is evident that irrigation water, soil, and possibly climate all influence the phosphorus content of wheat.

There is no direct relationship between the total and the inorganic phosphorus content of wheat. The Richfield wheat with

0.455% of total phosphorus contained only 3.3% of it as inorganic phosphorus; whereas the Hill Top grain containing only 0.205% of total phosphorus had 10.7% as inorganic phosphorus. With few exceptions the percentage of inorganic phosphorus is low and does not vary greatly in different samples.

TABLE IV

TOTAL AND INORGANIC PHOSPHORUS IN WHEAT FROM DIFFERENT SECTIONS OF UTAH

Locality	Total phosphorus	Inorganic phosphorus	Percentage of total phosphorus inorganic
	%	%	
Richfield	0.455	0.015	3.3
Vernon	.448	.021	4.7
Kamas	.444	.033	7.4
Grantsville	.442	.022	5.0
Coalville	.432	.027	6.2
Elberta	.430	.030	7.0
Lewiston	.415	.023	5.5
Wanship	.396	.028	7.1
Vernon	.392	.018	4.6
Payson	.390	.017	4.4
Beaver	.386	.026	6.7
Castle Dale	.380	.017	4.5
Henefer	.378	.026	6.9
Tooele	.372	.023	6.2
Santaquin	.367	.026	7.1
Heber City	.369	.040	10.8
Joe's Valley	.352	.024	6.8
Stockton	.351	.031	8.8
Ephraim	.346	.024	6.9
Price	.335	.015	4.5
Nephi	.326	.016	4.9
Fairview	.305	.024	7.9
Salina	.297	.013	4.4
Morgan	.293	.019	6.5
Spanish Fork	.270	.020	7.4
Nephi Substation	.209	.013	6.2
Hill Top	0.205	0.022	10.7

The total and inorganic phosphorus in oats from various sections is given in Table V.

There is a variation of 70% in total phosphorus content of oats grown in different localities, and a variation of 122% of inorganic phosphorus. There is, however, a closer correlation between the total phosphorus and the inorganic phosphorus of the oats than of the wheat. The inorganic phosphorus varies from 5.5% to 12.5% of the total phosphorus. There is a greater variation in the phosphorus content of oats because of the locality in which they were grown than because of the irrigation water. The phosphorus content of barley from different localities in Utah is given in Table VI.

TABLE V

TOTAL AND INORGANIC PHOSPHORUS IN OATS FROM DIFFERENT SECTIONS OF UTAH

Locality	Total phosphorus	Inorganic phosphorus	Percentage of total phosphorus inorganic
	%	%	
Spanish Fork	0.451	0.048	10.6
Koosharem	.437	.032	7.3
Henefer	.421	.047	11.2
Ephraim	.420	.043	10.2
Grantsville	.413	.036	8.7
Lewiston	.404	.051	12.6
Elberta	.395	.049	12.4
Beaver	.390	.042	10.8
Coalville	.385	.039	10.1
Kamas	.380	.036	9.5
Wanship	.383	.054	14.1
Morgan	.374	.021	5.6
Nephi	.373	.039	10.4
Santaquin	.369	.028	7.6
Payson	.369	.032	8.7
Vernon	.368	.033	9.0
Heber City	.351	.040	11.4
Ferron	.335	.036	10.7
Fairview	.268	.029	10.8
Nephi Substation	0.267	0.023	8.6

The variation in the total phosphorus of barley from the different localities is 87%. This is less than in wheat but slightly greater than in oats. The inorganic phosphorus shows a wide variation and is not correlated with the total phosphorus of the barley.

TABLE VI

TOTAL AND INORGANIC PHOSPHORUS IN BARLEY FROM DIFFERENT SECTIONS OF UTAH

Locality	Total phosphorus	Inorganic phosphorus	Percentage of total phosphorus inorganic
	%	%	
Morgan	0.444	0.051	11.5
Spanish Fork	.433	.036	8.3
St. John	.427	.044	10.3
Henefer	.407	.040	9.8
Kamas	.399	.044	11.0
Lewiston	.378	.040	10.6
Wanship	.367	.041	11.2
Coalville	.363	.042	11.6
Nephi	.341	.024	7.0
Vernal	.317	.031	9.8
Grantsville	.314	.029	9.2
Hill Top	.276	.021	7.6
Fairview	.270	.015	5.6
Nephi Substation	0.238	0.020	8.4

It is evident from these results that the total phosphorus of wheats, oats, and barley increases as the irrigation water applied during the growing stage increases. It also varies with the soil on which the grain was grown. The maximum, minimum, and

average phosphorus content of the different grains is given in Table VII.

TABLE VII

MAXIMUM AVERAGE, AND MINIMUM PHOSPHORUS CONTENT OF GRAINS GROWN IN DIFFERENT SECTIONS OF UTAH

	Wheat		Oats		Barley	
	Total	Inorganic	Total	Inorganic	Total	Inorganic
	%	%	%	%	%	%
Maximum	0.455	0.040	0.451	0.051	0.444	0.051
Average	.363	.023	.377	.037	.355	.034
Minimum	0.205	0.013	0.267	0.021	0.238	0.015

As an average, in wheat 6.3% of the total phosphorus was inorganic; in oats, 9.8%; and in barley, 9.6%. Corn grown under varying conditions of water and manure contained from 0.32% to 0.35% total phosphorus, from 12.2% to 16% of which was inorganic. Apparently the addition of barnyard manure to soil increases the proportion of inorganic phosphorus in the corn kernel.

Literature Cited

Association of Official Agricultural Chemists
1925 Official and tentative methods of analysis.

Forbes, E. B., Lehman, A., and Collison, R. C.
1910 Method for the quantitative estimation of inorganic phosphorus in vegetable and animal substances. Ohio Agr. Expt. Sta. Bull. 215:459-589.

Greaves, J. E. and Carter, E. G.
1923 The influence of irrigation water on the composition of grains and the relationship to nutrition. J. Biol. Chem. **58**:531-541.

CORRELATION BETWEEN DIASTATIC POWER OF FLOUR AND CRUST COLOR IN THE TEST LOAF, AND ITS SIGNIFICANCE[1]

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(Received for publication January 25, 1929)

It has long been generally known that depth of crust color in bread may be augmented by increasing the amount of sugar or sugar-producing substance (diastase) in the dough, assuming that other factors are unchanged. Blish and Sandstedt (1927) reported and discussed some general observations as to the symptomatic value of crust color variations among test loaves when baked according to the type of procedure that later was tentatively adopted as a standard baking test procedure by the American Association of Cereal Chemists (1928). Their report was, in effect, that when all the ingredients and environmental factors of the baking test are fixed, precisely controlled, and *are the same for all flours,* comparative crust colors serve as a very reliable index to the relative diastatic powers, respectively, of the flours themselves.

This observation assumes that crust color is due primarily to a caramelization of sugar in the dough during baking, the deeper colors being obviously correlated with the higher concentrations of sugar, when all other factors have been kept constant. Flours baked by the fixed experimental baking procedure frequently show pronounced differences in depth of crust color, despite the fact that all received the same amount of sugar and yeast, in the formula, as well as the same fermentation time and degree of temperature during fermentation and baking. If depth of color is a function of the concentration of residual sugar in the dough at baking time, it is apparent that there may be a variation in the amount of residual sugar in test doughs from various flours. As all received the same amount of sugar added in the dough, and as all other factors were presumably the same, one of two assumptions is justified. Either the rate of fermentation has varied in the different doughs, or extra sugar has been made available for certain flours to a greater degree than for others. The latter assumption seems the more reasonable of the two,

[1] Published with the approval of the director as Paper No. 71, Journal series, Nebraska Agricultural Experiment Station.

since, as has been amply demonstrated by Rumsey (1922) and others, flours may differ widely in their respective diastatic powers, whereas the rigid maintenance of fixed and uniform conditions of fermentation and baking minimizes the possibility of serious differences in rate of fermentation.

Blish and Sandstedt (1927) state, "It is interesting, altho in no way surprising, to note that when a series of miscellaneous flours was experimentally baked by this (fixed) method, we found an almost perfect positive correlation between crust color and diastatic value of the flour, the latter being estimated on separate portions of the flours, respectively. We believe that in this type of baking method, crust color furnishes almost as useful an indication of diastatic value as does a special diastatic value determination."

The present report is submitted primarily for the purpose of substantiating the previous statement, by offering adequate experimental data.

Experimental

Series I.—Eighty-four flours were experimentally milled from miscellaneous samples of Nebraska wheats, most of which were hard winter varieties. The flours were experimentally baked by the method suggested by Werner (1925), except that 5 grams instead of 2.5 grams of sugar was used in the formula. This modification was found advisable for *experimentally milled* flours, in accordance with the observation of Blish and Sandstedt (1927) that such flours are decidedly lower in diastatic power than they would be if produced by commercial milling procedure. When this deficiency is not compensated for by additional sugar, the doughs from such flours will not stand the 3½ hour fermentation period of 30° C., as specified by Werner (1925), and the gas-producing factor becomes exhausted to the extent that all will usually produce small, exceedingly pale loaves which do not allow any useful differentiation. The test loaves were allowed to dry thoroly, and were preserved for color comparisons.

The diastatic power of the individual flours was estimated by a colorimetric procedure that gives results corresponding closely to values obtained by the rather long and tedious, tho reliable, procedure suggested by Rumsey (1922), with a decided advantage in simplicity, convenience, and time saving. This method, based on the one proposed by Willaman and Davison (1924), is as follows:

In order to estimate the original reducing sugar content of the flour without the occurrence of diastasis during extraction, extract 5 grams of flour with 50 cc. water in an ice bath for 15 minutes. Filter

the extract, discarding the first few drops of the filtrate, which may be turbid or cloudy. Add 1 cc. filtrate to a mixture of 2 cc. saturated picric acid solution and 1 cc. saturated sodium carbonate solution. For flours of abnormally high sugar content use ½ cc. of the extract, and for extremely low sugar concentrations, use 2 cc. Graduated centrifuge tubes (15 cc.) are convenient containers in which to mix the flour extract with the picric acid and sodium carbonate. The tube containing the mixture is placed in a boiling water bath for 30 minutes, during which time the reddish color fully develops, the depth of color being proportional to the concentration of reducing sugars. The mixture is then cooled and diluted to 10 cc. with water. It is then compared in a colorimeter with a similarly treated standard solution of pure maltose made up so that 1 cc. equals 1 mg. maltose. Accuracy and reliability are enhanced by so diluting the standard that the color produced in it matches as closely as possible that in the unknown before the final colorimetric comparison is made. From this colorimetric comparison the original sugar content is estimated, and it may be conveniently recorded as milligrams of maltose per 10 gm. flour.

Another 5-gram portion of the same flour is extracted with 50 cc. water at 30°C., for one hour, during which time the flour-water suspension is agitated every 10 minutes by vigorously rotating the flask. At the end of the hour the suspension is allowed to settle for 10 minutes. It is decanted through a filter, the first few drops being discarded as before. From here on the procedure is the same as already described for the ice-water extract. The diastatic value is ascertained by subtracting the amount of reducing sugar found originally in the flour from the total at the end of the digestion with water for one hour at 30°C. It may be arbitrarily recorded (as is the case in this report) as milligrams of maltose produced by 10 gm. flour in one hour at 30°C.

A comparison of results secured by this procedure with those obtained by Rumsey's (1922) copper reduction method is shown for five flours, as follows:

Sample	Colorimetric method mg. maltose per 10 gm. flour	Copper reduction method
6	107	114
901	123	124
16	102	104
33	138	146
995	80	74

The test loaves from the 84 flours in Series I showed such a wide range of crust color that they could be conveniently classified into 9 groups, ranging from the palest in group 1 to the darkest in group 9.

The loaves were grouped independently by two workers, and in certain "border line" cases where agreement as to classification was difficult, a third person made the decision. The correlation between crust color and diastatic value, as determined for this series, is indicated in Table I.

TABLE I

CORRELATION BETWEEN CRUST COLOR AND DIASTATIC VALUE, USING FIXED BAKING METHOD WITH 5 GM. SUGAR

mg. maltose per 10 gm. flour	Groups of increasing depths of crust color									
	1	2	3	4	5	6	7	8	9	Total
25	2	....	....	....	....	....	....	....	....	2
50	2	2	11	....	....	....	....	....	....	15
75	4	....	18	3	....	....	....	....	....	25
100	1	....	11	3	4	....	....	....	....	19
125	....	1	9	2	1	....	1	....	....	14
150	....	....	1	....	....	1	....	....	....	2
175	....	....	....	....	....	....	....	....	1	1
200	....	....	....	....	1	....	2	1	1	5
225	....	....	....	....	....	....	....	....	1	1
	9	3	50	8	6	1	3	1	3	84

$r = +0.75 \pm .03$

The correlation coefficient of 0.75, as shown in Table I, indicates a strongly positive correlation between crust color and diastatic activity in Series I. That the coefficient is not even higher is doubtless due in part to border-line cases in which there was doubt as to the group in which certain samples should have been placed. Furthermore, there were occasional instances in which the true color was masked by a tendency toward a cloudy or "mottled" appearance of the top crust. This was especially noticeable among the flours of low protein content. Such a condition is also common in flours that have been "over-oxidized," either by aging, by artificial bleaching, or by excessive use of "yeast foods" containing oxidizing agents. No bleaching or oxidizing agents were deliberately used in Series I, however. This condition adds to the difficulty of assigning true crust color values to test loaves, especially in the border-line cases.

Series II.—In the next series of experiments, the correlation between crust color and residual sugar in the baked loaf was estimated. The loaves were baked as in Series I. Residual sugar was determined colorimetrically in the dried bread, and recorded arbitrarily as dextrose. The 46 flours employed in this series showed a much narrower range of color variation than those in Series I, and the test loaves were accordingly classified into only four groups, instead of nine. Furthermore, there were more border-line cases than in Series I. This presented greater difficulty in classifying them by mere inspection. Table II indicates the result of this experimental series.

TABLE II

CORRELATION BETWEEN CRUST COLOR AND RESIDUAL SUGAR IN THE BAKED TEST LOAF

Residual sugar as per cent dextrose in dried bread	Groups of increasing depths of crust color				
	1	2	3	4	Total
1.5	4	6	1	1	12
2.5	....	6	2	3	11
3.5	....	....	12	2	14
4.5	....	....	4	5	9
	4	12	19	11	46

$r = +0.65 \pm .06$

The correlation coefficient 0.65 ± 0.06 establishes beyond reasonable doubt the positiveness of correlation between crust color and residual sugar in the test loaf. It is believed that in this series the comparatively larger number of border-line cases caused the correlation coefficient to be slightly smaller than in Series I.

Series III.—In this series 105 flours were baked without the use of any sugar in the formula, this being partially compensated for by reducing the fermentation period from 3½ hours to one hour. Crust color variations, therefore, reflected almost exclusively the differences in the fermentable sugars present in or produced by the flours themselves. The loaves were classified into 5 groups, according to crust color. The correlation between crust color and residual sugar is shown in Table III.

TABLE III

CORRELATION BETWEEN CRUST COLOR AND RESIDUAL SUGAR IN TEST LOAVES BAKED WITHOUT ADDED SUGAR

Color groups	Residual sugar as per cent dextrose in the dried bread						
	0.75	1.25	1.75	2.25	2.75	3.25	Total
5	...	...	...	3	6	...	9
4	...	2	...	6	1	...	9
3	...	2	4	...	1	...	7
2	6	16	...	1	...	...	23
1	56	1	...	...	...	...	57
	62	21	4	10	8	...	105

$r = +0.73 \pm .03$

Series IV.—This series involved the same flours and the same test loaves as in Series III. The correlation studied, however, was that between crust color and diastatic activity, as in Series I. The nature of the correlation here found is shown in Table IV.

TABLE IV

CORRELATION BETWEEN CRUST COLOR AND DIASTATIC VALUE, USING TEST LOAVES BAKED WITHOUT ADDITION OF SUGAR

Color groups	Diastatic value (mg. maltose per 10 gm. flour)				
	25	75	125	175	Total
4	...	1	4	3	8
3	...	6	13	2	21
2	...	60	9	...	69
1	2	4	...	...	6
	2	71	26	5	104

$r = +0.703 \pm .03$

Discussion

The coefficients of correlation found in all four series show that crust color is positively correlated with residual sugar in the baked test loaf on the one hand and with the diastatic power of the flour on the other, providing all factors of the baking test are fixed, carefully controlled, and the same for all flours. These correlation coefficients ranged from 0.65 to 0.75. That the coefficients are not higher is probably due largely to errors of personal judgment in color classification, which was done merely by inspection. In many instances differences in apparent color depth were so small that it was very difficult to decide into which group the loaf should be placed. However, where color differences were sharp and unmistakable, the order of color depth was invariably directly proportional to both diastatic power and residual sugar in the baked loaf.

In each series test loaves were occasionally encountered in which the true depth of color was somewhat masked by a dull grayish or "mottled" appearance, noticeable especially on the top crust. As previously mentioned, this effect was noted particularly in flours of low protein content, and it strongly resembled a characteristic manifestation occurring in flours that have been over-oxidized, either by aging, bleaching, or the excessive use of yeast foods containing oxidizing agents. This item can easily cause errors in the classification of crust color, and was doubtless a factor of error in these experiments.

All things considered, these experiments afford ample foundation for a belief that crust color serves as a reliable index to the diastatic value of flour when test loaves are produced under fixed, uniform, and carefully controlled conditions. Its reliability is amply sufficient for practical purposes, for in all cases where differences in crust color were clear and unmistakable they were positively correlated with both residual sugar in the loaves and the diastatic power of the flours under consideration.

Blish and Sandstedt (1927) have reported that in their experience "fermentation tolerance" in bread baking depends more upon the maintenance of sufficient gas production (implying an ample sugar supply) during panary fermentation than upon the nature of the gluten, or gas-retaining factor. This is doubtless an important reason why the sponge-dough method of bread making (in which the sugar is incorporated almost immediately preceding the panary fermentation) is more fool proof than the straight dough method. When handled by the straight dough method, flours vary widely as to their relative fermentation tolerance.

If it be true that fermentation tolerance depends more upon sustained gas production than upon gluten quality, it follows that variations in fermentation tolerance must be directly proportional to corresponding variations in diastatic power. As crust color may be made to serve as a reliable index to diastatic power, it should serve equally well as an indicator of relative fermentation tolerance among flours. This should allow a reasonably reliable estimation of relative fermentation tolerance from but one test bake, which tends to eliminate the necessity for making several bakes in which the fermentation time is varied, as is frequently done in laboratory flour testing.

Summary

When all flours are experimentally baked by the same specified and fixed procedure, in which all environmental factors are precisely controlled, depth of crust color is positively and definitely correlated with residual sugar in the baked loaf on the one hand and with relative diastatic power and fermentation tolerance of the flour on the other.

Literature Cited

Blish, M. J.
1928 Standard experimental baking test. Cereal Chem. 5:158-161.
Blish, M. J. and Sandstedt, R. M.
1927 Factors affecting interpretation of experimental baking tests. Cereal Chem. 4:291-299.
Rumsey, L. A.
1922 The diastatic enzymes of wheat flour and their relation to flour strength. Am. Inst. Baking, Bull. 8.
Werner, E. E.
1925 The baking test. Cereal Chem. 2:310-314.
Willaman, J. J. and Davison, F. R.
1924 Some modifications of the picric acid method for sugars. J. Agr. Research 28:479-488.

MANGANESE IN CEREALS AND CEREAL MILL PRODUCTS[1]

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(Received for publication, December 24, 1928)

Introduction

Much attention has been given in recent years to the elements found in plant and animal tissues in relatively small quantities, and as a result some of the elements formerly considered non-essential in plant and animal metabolism have now been transferred to the list of essential elements. Bertrand (1926), for instance, having found cobalt and nickel in insulin, claims to have used these elements in the treatment of diabetes with a moderate degree of success. Boron (Brenchley and Warington, 1927) and manganese (McHargue, 1924) have been found to be necessary for the normal development of many plants.

The functions of these new additions to the list of essential elements have not yet been determined. Manganese, however, has been studied much more than the other elements of this group. It has been found that the manganese content of many plants is directly related to the intensity of their oxidase activity (Bertrand, 1897), (McHargue, 1914). McHargue (1922) has shown that manganese is necessary for the formation of chlorophyll in some plants, its function being analogous to that of iron. The analogy of function between these two elements is further strengthened by the fact that manganese has been found helpful in the therapy of anemia (Wood and LaWall, 1926), in the treatment of which iron has long been used. As the result of another investigation, in which he found a relative abundance of manganese in the plant and animal tissues that are rich in vitamins, McHargue (1914) came to the conclusion that the action of this element is closely associated with that of the vitamins. McCarrison (1927), having studied the comparative nutritive values of whole wheat and whole rice, also came to the conclusion that the growth-promoting properties of whole wheat are partly due to its manganese content.

The object of the work reported in this paper was to study the variation in the manganese content of cereals of several varieties, and

[1] Presented at the Seventy-fifth Meeting of the American Chemical Society, St. Louis, Mo., April 19, 1928.

of some of their extraction products, in relation to ash and protein content.

Materials and Methods

Five varieties of each cereal were used for analysis.[2] To eliminate the effect of local and yearly variations, the specimens of each cereal were selected from the harvest of the same year, and most of them from the same locality.

From 5- to 10-gram samples of the ground grains were used for ash and manganese determinations. One-gram samples were used for nitrogen determinations. Manganese was determined by the periodate method as outlined by the Association of Official Agricultural Chemists (1925).

All determinations were made in duplicate on samples ashed for the most part on different days. A Schreiner colorimeter was used for comparisons with the standard permanganate solutions. The duplicate determinations agreed closely.

Results

Correlation between manganese and ash might be expected, as manganese is a part of the total ash. The study of the correlation between manganese and protein was suggested by results obtained in this laboratory on wheat from plots to which sodium nitrate had been added at different stages of growth and which indicated that the manganese content is inversely related to the protein content (Table I).

TABLE I

MANGANESE, ASH, AND PROTEIN IN WHEAT THAT RECEIVED AN APPLICATION OF SODIUM NITRATE AT HEADING TIME

Wheat	Distance between rows	Manganese (Mn_3O_4)*	Ash*	Protein (N x 5.7)*
	in.	per cent	per cent	per cent
Control	8	0.0119	1.85	10.7
Sodium nitrate applied at heading time	8	.0091	1.68	12.5
Sodium nitrate applied at heading time	24	0.0076	1.71	13.2

*Air dry basis

The data obtained in the present work (Table II) show, however, that the manganese content of the different varieties of cereals does not vary consistently with the fluctuations in the ash content, except in the hard winter wheats. Moreover, no correlation was found between the manganese and protein in the varieties of one cereal, notwithstanding the fact that some of the differences in the

[2] The writer is indebted to J. A. Clark, C. E. Leighty, H. V. Harlan, T. R. Stanton, F. D. Richey, and C. E. Chambliss, all of Cereal Crops and Diseases, Bureau of Plant Industry, United States Department of Agriculture, for their kindness in furnishing the grains.

protein content, especially of the wheats, were greater than those of the wheat obtained from the experimental plots of this labora-

TABLE II

MANGANESE, ASH, AND PROTEIN IN CEREALS*

Cereal	Place grown	Year	Manganese	Ash	Protein
			per cent	per cent	per cent
Hard winter wheat					
Kanred	North Platte, Nebr.	1927	0.0034	1.921	15.6
Karmont	North Platte, Nebr.	1927	.0034	2.105	17.2
Minturki	North Platte, Nebr.	1927	.0052	2.269	18.2
Buffum No. 17	North Platte, Nebr.	1927	.0068	2.344	19.8
Turkey	North Platte, Nebr.	1927	.0052	2.152	17.6
Soft winter wheat					
China	Arlington Farm	1927	.0086	1.935	12.3
Currell	Arlington Farm	1927	.0086	2.002	10.8
Red Rock	Arlington Farm	1927	.0086	1.808	16.5
Leap	Arlington Farm	1927	.0086	1.816	14.2
Fultz	Arlington Farm	1927	.0086	1.799	12.5
Hard red spring wheat					
Marquis	Dickinson, N. D.	1926	.0052	1.798	14.6
Ruby	Dickinson, N. D.	1926	.0052	1.713	14.0
Red Bobs	Moccasin, Mont.	1926	.0047	1.613	19.0
Ceres	Dickinson, N. D.	1926	.0060	1.738	17.6
Reliance	Moccasin, Mont.	1926	.0034	1.746	16.9
White spring wheat					
Quality	Pullman, Wash.	1926	.0068	2.026	14.1
Pacific Bluestem	Aberdeen, Idaho	1926	.0086	2.018	14.0
Federation	Aberdeen, Idaho	1926	.0068	1.660	13.6
Hard Federation	Aberdeen, Idaho	1926	.0086	1.723	15.8
Baart	Aberdeen, Idaho	1926	.0086	1.907	16.7
Rye					
Von Rumker	Arlington Farm	1927	.0105	2.052	11.7
Rimpau	Arlington Farm	1927	.0122	2.062	10.6
Star	Arlington Farm	1927	.0157	2.028	9.5
Rosen	Arlington Farm	1927	.0110	2.187	9.6
Abruzzes	Arlington Farm	1927	.0121	1.969	11.2
Corn					
North Dakota white flint	North Dakota	1926	.0009	1.644	11.7
Huffman	Tennessee	1926	.0009	1.440	8.5
Northwestern dent	North Dakota	1926	.0009	1.616	11.7
Iodent	Iowa	1926	.0009	1.545	10.3
Boone County white	Virginia	1926	.0018	1.519	10.0
Rice					
Fortuna	Crowley, La.	1927	.0043	1.510	8.0
Early prolific	Crowley, La.	1927	.0052	1.298	7.6
Edithe	Crowley, La.	1927	.0043	1.569	8.8
Lady Wright	Crowley, La.	1927	.0043	1.449	8.0
Blue Rose	Crowley, La.	1927	.0061	1.132	8.2
Oats					
Iowan	Dickinson, N. D.	1927	.0076	4.176	14.8
Richland	Dickinson, N. D.	1927	.0066	3.696	14.8
Red Rustproof	Arlington Farm	1927	.0204	3.947	11.0
Markton	Dickinson, N. D.	1927	.0067	3.945	11.9
Silvermine	Dickinson, N. D.	1927	.0067	3.995	14.8
Barley					
Smyrna	Aberdeen, Nebr.	1925	.0012	2.352	13.0
Meloy	Aberdeen, Nebr.	1925	.0020	3.264	12.3
Algeria	Aberdeen, Nebr.	1925	.0020	2.565	14.0
Orel	Aberdeen, Nebr.	1925	.0020	2.902	13.9
Horn	Aberdeen, Nebr.	1925	0.0018	2.469	13.9

*Moisture free basis.

tory, mentioned above. The same lack of correlation was found between the protein content and the manganese content of different cereals. The barleys and the oats, for instance, have about the same protein content, but the manganese content of the oats is from three to six times as high as that of the barleys.

When the types of wheat are considered collectively, however, a distinct *inverse* relation between manganese and protein is found. The hard winter wheats and the red spring wheats have a higher protein content and a lower manganese content than the soft winter wheats and the white spring wheats.

Barley and corn, especially corn, are much lower in manganese than the other cereals studied. Boone County White corn, grown on the Arlington Farm, had twice as much manganese as the other varieties, but this may be due to the effect of locality. The manganese content of the Red Rustproof oats, also grown on the Arlington Farm, was about three times as high as that of the other varieties of this cereal.

Altho there is, according to Bertrand (1897) and McHargue (1914), a direct relation between the manganese content of plants and their oxidase activity, there seemed to be no correlation between the manganese content of the cereals as determined in this investigation and their diastatic properties as quoted by Levy (1899) from Moralsky and Glaser (Table III). The barleys, with a relatively low manganese content, serve as the principal source of commercial malt, which has as high diastatic properties as the malt from rye and wheat. On the other hand, corn, which has the lowest manganese content of all the cereals studied, and oats, which has a relatively high manganese content, have equally low diastatic properties.

TABLE III

MANGANESE CONTENT OF CEREALS AND ITS RELATION TO THE RELATIVE DIASTATIC STRENGTH OF THEIR MALTS

Cereal	Manganese (Mn_3O_4)	Relative diastatic strength of malts
	per cent	
Barley	0.0012–0.0020	100.0
Rye	.0105– .0157	93.1
Wheat	.0034– .0086	107.0
Oats	.0067– .0204	30.0
Corn	0.0009–0 0018	28.9

Most of the manganese values obtained in this work are much higher than those reported by Lindow and Peterson (1927), who determined the manganese content of wheat, oats, corn, and barley, and of 79 other plant and animal foods. These higher values may be

owing to the varieties and source of the cereals studied, as the manganese content of cereals differs with variety (Table II) and probably with locality.

Manganese, Ash, and Protein in Cereal Extraction Products

By way of comparison, manganese was also determined in the milling products of wheat and in some of the widely used breakfast foods, and its relation to the ash and protein content was considered.

The results (Table IV) show in a general way a correlation between the ash and the manganese content. The cereal products that are relatively poor in ash are also poor in manganese, the low content of both being evidently due to the removal of the germ and the outer parts of the grain in the process of preparation.

TABLE IV

MANGANESE, ASH, AND PROTEIN IN CEREAL EXTRACTION PRODUCTS*

Cereal product	Manganese (Mn_3O_4)	Ash	Protein (N x 5.7)	Moisture
	per cent	per cent	per cent	per cent
Bran†	0.0432	7.27	14.5	11.88
Shorts†	0465	4.07	15.2	9.88
Flour†	.0027	0.57	11.0	12.45
Wheat breakfast food No. 1	.0052	1.44	11.0	9.10
Wheat breakfast food No. 2	trace	0.50	11.5	12.82
Wheat breakfast food No. 3	.0072	1.93	10.3	12.41
Rolled oats	.0052	2.13	13.8	9.67
Flaked corn	none	2.81	7.1	4.93
Uncoated rice	.0011	0.37	7.1	12.88
Pearl barley	0.0004	0.65	7.0	9.22

*Moisture-free basis.
†From a purple straw wheat rich in manganese.

Cornflakes form an apparent exception, having a high ash content and no manganese. The ash content is, however, much higher than that of whole corn, indicating that the ash is largely salt introduced in the process of manufacturing.

No correlation was found between the manganese and the protein in the cereal extraction products, except in the milling products of wheat.

It is noteworthy that both uncoated rice and corn, which are associated with the nutritional deficiency diseases beri-beri and pellagra, are extremely poor in manganese.

Summary

Manganese, ash, and protein were determined in five varieties of each of the following cereals: Hard winter wheat, soft winter wheat, red spring wheat, white spring wheat, rye, corn, rice, oats, and barley. Similar determinations were made on some of their extraction products.

No correlation was found between the manganese and the ash content either in the varieties of one cereal or in different cereals. Neither was any correlation found between manganese and protein, except when the types of wheat are considered collectively. In that case the relation was inverse, the hard winter and red spring wheats being higher in protein and lower in manganese, than the two types of soft wheat.

The manganese content of Red Rustproof oats grown in Arlington was several times higher than that of oats of the other varieties studied.

There was no distinct correlation between the manganese content and the protein content of the cereal products, with the exception of the milling products of wheat. The products having a low ash content also had a low manganese content, both being due to the low degree of extraction.

The results indicate that there is no correlation between the manganese content and the diastatic properties of the cereals studied.

Corn and uncoated rice, which are associated with nutritional deficiency diseases, were both low in manganese.

Literature Cited

Association of Official Agricultural Chemists
1925 Official and tentative methods of analysis, 2d. ed. p. 42. Washington, D. C.

Bertrand, Gabriel
1897 Sur l'intervention du manganèse dans les oxidations provoqées par la laccase. Compt. Rend. 124:1032-1035.
1926 The importance of minute chemical constituents of biological products: Nickel, cobalt and insulin. Science 64:629-630.

Brenchley, W. E. and Warington, Katherine
1927 The rôle of boron in the growth of plants. Ann. Bot. 41:167-187.

Levy, Lucien
1899 La pratique du maltage. p. 149. Georges Carre et C. Naud, Editeurs. Paris.

Lindow, C. W., and Peterson, W. H.
1927 The manganese content of plant and animal materials. J. Biol. Chem. 75:169-175.

McCarrison, R.
1927 Effect of manganese on growth. Indian J. Med. Research 14:641.

McHargue, J. S.
1914 The occurrence and significance of manganese in the seed coat of various seeds. J. Am. Chem. Soc. 36:2532-2536.
1922 The rôle of manganese in plants. J. Am. Chem. Soc. 44:1592-1598.
1924 The association of manganese with vitamins. J. Agr. Research 27:417-424.

Wood, H. C., and LaWall, C. H.
1926 The dispensatory of the United States of America. 21st ed. pp. 1373-1374. J. B. Lippincott Co., Philadelphia.

HYGROSCOPY IN FLOUR ASH AND A DISCUSSION OF DIRECT ASH WEIGHING

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(Received for publication, November 13, 1928)

The necessity of good desiccation in the cooling of crucibles containing flour ash and of rapid weight determinations soon after the crucibles have attained room temperature is an accepted fact among cereal chemists. However, there has been a serious discussion as to the deliquescent properties of flour ash and the possibility of exact determinations of ash content by weighing the ash directly on a scale-pan on the balance. This method is used in some of the laboratories in the Southwest, especially in Kansas, and the writer was interested in determining the relative merits of results obtained by correlation with results obtained by the standard A.O.A.C. method as given in "Methods for the Analysis of Cereals and Cereal Products" (page 38). For this purpose more than 200 analyses were made of every type of flour available, both northwestern and southwestern milled, ranging in grade from high patents to low grades of soft and hard wheats, and including some phosphated samples, by both methods under various conditions and the results were summarized.

Before beginning a discussion of results, the method used will be described. A 3-gram sample of flour to be tested is weighed in an aluminum scoop, then dumped into a clean crucible and ignited in the usual manner. On being removed from the muffle the crucibles are allowed to cool to room temperature in a desiccator. (Calcium-carbide was used as the desiccating agent.) The ash is then dumped directly on a scale-pan and weighed. Crucibles used were of the low-form type of fused silica of about 12 cc. capacity. The muffle furnace was not automatically controlled, but kept a fairly constant temperature of about 525°C. The time allowed for ignition was in most cases 5 hours except for spring wheat flours, which required a longer time. Other runs were made with 16 hours ignition at a slightly lower temperature.

Uniformity of results is the one great aim of the ambitious analyst, and the discovery and elimination of any factors interfer-

ing with that uniformity are always desirable. It has been noticed by every observing ash analyst that the crucibles weigh less before they attain room temperature than soon after, and that they continue to gain weight. Nutting[1] suggests that the decrease in weight of heated solids is not due to temperature or convection currents in the balance but to layers of warm air in contact with the heated surface that are at the same pressure as the surrounding atmosphere but less dense and more viscous, hence are weakly adsorbed by the solid and lightly held in position, effecting an increase in the volume of the solid and therefore enhancing the buoyancy of the surrounding air.

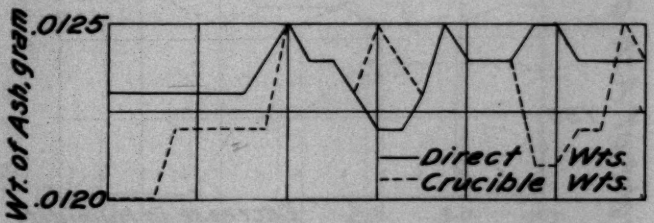

Fig. 1. Relation of Direct Weights of Flour Ash to Weights of Ash in Crucibles for Consecutive Analyses of the Same Sample

It has been observed by the writer, however, that the relative humidity of the air in the laboratory exerts a greater influence upon the weight of a crucible than the temperature at which the crucible is weighed, especially when the temperature of the crucible is allowed to become less than the temperature of the room. As any variation in the weight of a crucible produces an error in the weight of the ash, this factor would be eliminated by weighing the ash directly, provided this weight is dependable and uniform. To determine this, a sample of flour was withdrawn daily for a period of one month from a lot of flour preserved in a corked bottle to insure uniform moisture content, and the apparent ash content of the sample was determined. The resulting data are recorded in Figure 1 and show that not only did the direct ash weights check those made in crucibles but on the whole were more uniform. It was observed that where the weight of the ash from the crucible was less than that of the direct ash the relative humidity of the air was greater at the time of the initial weighing of the crucible than at the final weighing. This is in accordance with the previous statement as to the effect of humidity on the weight of a crucible, because if the first weight of the crucible alone should be greater than

[1] Science 66:652 (1927).

the second weight, the amount of calculated ash would be less than the actual amount.

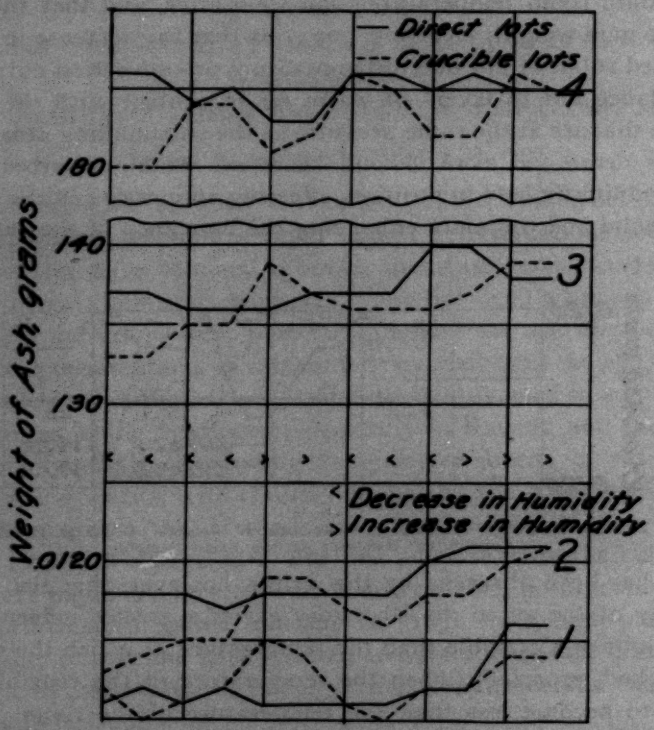

Fig. 2. Relation of Ash Weights Determined by Direct Weighing and by Weighing in Crucibles for Four Grades of Flour

Figure 2 records the results of consecutive ash determinations made from the same samples of (1) a soft wheat patent flour, (2) a hard wheat patent, (3) a hard wheat straight, and (4) a hard wheat clear. In this graph it may be noticed again that the direct ash weights are more uniform than those made in crucibles, and that, also, with a decrease in relative humidity the crucible ash weighs less than the direct ash; i.e., when the relative humidity of the laboratory air is greater at the first weighing of the crucible than at the final weighing, the initial weight of the crucible is high and therefore the calculated weight of the ash is too low. This, then, might lead to a misconception of the true ash content of the flour. However, in all cases the results check within the limits of experimental error.

The barometric pressure of the laboratory air was recorded with each set of determinations but seemed to have no relation to

the crucible weights except as it varied with the moisture content of the air. Twelve samples of the same flour were ashed together, then cooled for 10 minutes in the desiccator, and one was weighed after each interval of 3 minutes. The results, as recorded in Figure 3, show that over a range of more than 30 minutes the ash does not gain appreciably in weight; i.e., enough to surpass the limits of experimental error. Also, after the ash has apparently gained 0.0004 gm. of moisture the weight remains constant exactly; hence the deliquescence of the ash introduces an error of only about 3% of the total.

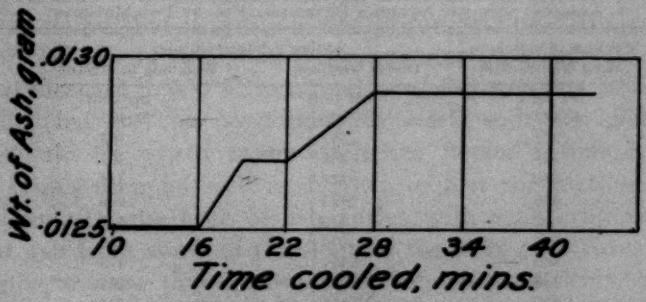

Fig. 3. Effect of Time of Cooling in the Desiccator on Direct Weights of Flour Ash Showing Hygroscopic Properties of the Ash

TABLE I
WEIGHT OF FLOUR ASH AS WEIGHED DIRECTLY, AND IN CRUCIBLES

		Direct crucible difference			
gm.	gm.	mgm.	gm.	gm.	mgm.
	Soft wheat patent			Hard wheat patent	
0.0110	0.0110	0	0.0126	0.0126	0
.0110	.0111	−1	.0121	.0123	−2
.0118	.0116	+2	.0124	.0124	0
.0119	.0119	0	.0123	.0120	+3
.0103	.0102	+1	.0125	.0124	+1
.0104	.0101	+3	.0125	.0125	0
	Hard wheat straight			Hard wheat clear	
.0134	.0130	+4	.0183	.0181	+2
.0133	.0131	+2	.0181	.0180	+1
.0136	.0138	−2	.0198	.0198	0
.0130	.0127	+3	.0185	.0182	+3
.0133	.0133	0	.0204	.0206	−2
.0132	.0133	−1	.0205	.0206	−1
	Northwestern Flour			Phosphated Flour	
.0149	.0148	+1	.0306	.0310	−4
.0148	.0148	0	.0309	.0310	−1
.0150	.0149	+1	.0330	.0333	−3
.0150	.0149	+1	.0280	.0282	−2
.0137	.0138	−1	.0330	.0333	−3
0.0136	0.0138	−2	0.0280	0.0284	−4

Table I gives the results of analyses taken at random from the complete list of analyses, as too much space would be required to print the entire list and these are representative of all. The

average deviation of the complete list of direct weights from those made in crucibles was only 0.00026 gm.—a variation of 0.00862% in the result of the calculated ash.

In order to check the accuracy of these results, samples were exchanged with three other laboratories in Kansas City. The results are given in Table II. The first result is that of a sample sent by the Kansas City section of the A.A.C.C. to its member laboratories for check analyses.

TABLE II

COMPARISON OF AVERAGE RESULTS OF ASH DETERMINATIONS MADE BY SEVERAL COLLABORATING ANALYSTS WITH THE AUTHOR'S DETERMINATIONS BY TWO METHODS

Average of collaborating laboratories	Author's determinations	
	Direct weighing	Weighing in crucible
per cent	per cent	per cent
0.427	0.432	0.437
.375	.382	.383
.365	.368	.367
.378	.375	.373
.410	.423	.430
.412	.420	.420
.600	.630	.623
.465	.477	.473
.430	.440	.442
.420	.425	.427
0.413	0.420	0.423

An apparent possible objection to depending on direct weights is that all the ash might not be removed from the crucible. Most of the incinerations in this work were conducted in vitreosil crucibles and no difficulty was ever experienced in the instant removal of the entire ash by a tap of the finger on the bottom of the inverted crucible. Phosphated flour ash at times showed a tendency to "splatter," but was rapidly and completely removed with the tip of the spatula. Some of the flour samples were also incinerated in porcelain and in platinum crucibles with identical results, so that the composition of the crucible apparently had no effect on the results. It was found, however, that if the porcelain crucibles were placed in the furnace having a temperature much above 500°C., the ash showed a slight tendency to stick, also that after a few dozen ignitions the crucibles became worthless. Fused silica crucibles seem to be ideal for the samples of flour during ignition. The characteristic performance of an efficient balance operator would eliminate the possible errors introduced by failure to brush the scale-pan perfectly clean after each weighing, and to wipe all crucibles free from dust and dirt before a new sample of flour is introduced into it.

Certainly a point in favor of the method, in any laboratory where a large number of ash determinations must be made, is the factor of average time consumed for each determination. It was the experience of the writer that less than half the usual amount of time was required for a line of direct ash determinations. If one man must weigh out ash from the initial crucible weights of another, the personal factor of error is introduced. This is eliminated by use of the direct method.

The analyses recorded here were made on flour from the 1927 crop of wheat, and the ash was fluffy even with spring wheat flours, tho it was found that if ignition was begun around 550°C. the ash was much smaller in bulk than if ignition started about 450°C. with a gradual increase to 600°C. as a final temperature for a 5-hour run. The writer has had no opportunity to work with the 1928 flour, and it would be worth some interested person's time to work on this crop's flour as well as further to test the method. It is well known that the type of ash varies with each crop and it is said that ash from some of the flour of the 1928 crop fuses easily. This seems to show that, according to Johnson and Scott,[2] the ash contains the right percentage of pyro- and meta-phosphates to form a eutectic mixture of low fusion point. This method could not be used for flour that gave a fused ash, nor is any method exact for a fused ash. However, an ash slightly stuck to the bottom of a crucible may be entirely removed with the tip of a spatula.

Summary

Uniformity of results is the aim of every analyst. The elimination of factors interfering with this is desirable. Variations in the weight of crucibles introduce errors. Direct weights of the ash would eliminate this, if direct weights are reliable. The reliability of these weights is shown in graphs and tables. The hygroscopic tendencies of flour ash affect the results very little in the period of time required for weighing the ash. It is the opinion of the author that there is the possibility of the development of a rapid and accurate method of technic in the determination of ash in flour by direct weighing.

Acknowledgment

The writer wishes to acknowledge his gratitude to R. K. Durham, E. L. Von Eschen, and P. P. Merritt, who kindly reviewed and criticized the manuscript. Mr. Von Eschen also aided by doing some check work in his laboratory.

[2] Cereal Chem. 5:56 (1928).

THE EFFECT OF DRY SKIMMILK UPON THE WATER ABSORPTION OF DOUGHS AND THE PLASTICITY OF FLOUR SUSPENSIONS[1]

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(Received for publication Nov. 5, 1927)

The "absorption" or water-imbibing capacity of bread doughs is of primary concern to the baker. A proper adjustment of the proportion of water is necessary to maintain the normal level of fermentation in doughs, and that stability which insures bread of good texture. Variations in absorption of flours from different sources is of interest because of its relation to the yield or quantity of bread by weight that can be produced from a unit weight of flour. Mangels (1928) computed the coefficient of correlation of water-absorbing capacity of flour, and weight of loaf baked from a unit weight of flour, and the average for four seasons, $r = +0.73 \pm 0.02$, demonstrated the value of high absorption to the baker.

When any modifications of the dough formula are attempted by the baker it is essential that the necessary adjustments in absorption be made at the same time, particularly when materials having a substantial water-imbibing capacity are involved. Thus when the baker approaches the problem of incorporating dry skimmilk in a dough, he is immediately confronted with the necessity of determining the quantity of water required by each unit of added dry milk.

Several methods have been suggested of measuring the "consistency" or relative plasticity of doughs. Obviously the trial and error procedure of mixing a number of doughs with varying proportions of water, noting the properties of the dough during fermentation and the characteristics of the baked loaf should yield a useful measure of the optimum absorption for a flour. This method fails to return any measure of the relative plasticity of the dough which yielded superior bread, however.

Jago and Jago (1911) and others have described viscometers that comprised a cylinder in which the dough was placed, a standard

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1 Published with the approval of the Director, as Paper No. 837, Journal Series, Minnesota Agricultural Experiment Station. Condensed from one section of a thesis presented by the American Dry Milk Institute Fellow, J. L. St. John, to the faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The authors are glad to express their thanks to the American Dry Milk Institute for the aid extended in supporting the fellowship under which this research was conducted.

aperture through which it was forced, and a weighted plunger that exerted pressure on the dough. The time required to force a unit quantity of dough through the aperture was the index of plasticity recorded with such instruments.

Briggs (1918) invented the "perfekdo" viscometer. A graduated glass tube was provided, one end of which was placed in contact with the dough surface. The other end was attached to a tank in which the air pressure had been reduced below that of the atmosphere. The rate at which the dough flowed through the tube constituted a measure of its plasticity.

Chopin (1921) devised an extensimeter equipped with a manometer, which recorded the force required to extend the surface of a thin sheet of dough. With stiff doughs of low mobility this force would be large, decreasing as unit increments of water are added to the dough formula.

Harrel (1927) described a gravimetric penetrometer which was so constructed that it could fall for a considerable distance before it encountered the dough surface. The distance that it penetrated varied with the percentage of water in the dough. A serious difficulty in the laboratory application of this device lies in the large quantity of dough required for the test. It is best adapted for use with a commercial dough.

Each of these devices represents the application of a different mechanical principle. None of them have come into sufficiently general use to be regarded as a standard device or method.

Power Consumption

It seems reasonable to assume that if the consistency of a dough be varied, it might be possible to make comparative measurements of these variations by determining the power required to operate a mechanical dough-mixing machine in which the dough is contained. To test this assumption, a watt meter was attached to the small dough-mixing unit consisting of a Werner-Pfleiderer mixing machine, clutch, gears and 1/6 horse-power motor. Doughs were made with 350 grams of flour, 10.5 grams each of sugar and yeast, 6.1 grams of salt, and 5.25 grams of shortening. When dry skimmilk was used, it was first reconstituted with 50 cc. of water and allowed to stand the length of time indicated in the tables.

The wattage of the empty unit, or the power requirement of the motor, gears, and mixing machine containing no dough, was first observed. This value was subtracted from the wattage of the unit with dough in the mixing machine, and the difference was recorded

as the power required to move the blades of the mixing machine through the dough. It is this difference to which reference is made as the "power requirements."

With all the ingredients in the mixing machine, it was observed that the power requirement increased rapidly during the first 15 seconds that the machine was operated, followed by a gradual increase for several minutes. This is evident from the data recorded in Table I. It accordingly becomes necessary to insure that readings that are used as a basis for the comparison of doughs be taken at the conclusion of a definite number of minutes of mixing, and for this purpose it was believed that useful results could be obtained after 6 minutes of operation of the small mixing machine.

TABLE I

EFFECT OF TIME DRY SKIMMILK STANDS AFTER RECONSTITUTION ON POWER CONSUMED IN MIXING

Time of standing hr.	Watts consumed after mixing for various lengths of time (minutes)										
	1–2	2	4	6	8	10	12	14	16	18	20
2	90	130	115	140	140	155	165	155	140	130	
3	90	110	120	135	140	165	170	155	155	140	
4	90	110	120	130	150	160	160	...	135	130	
5	80	100	115	125	125	145	145	135	130	130	
8	75	100	110	120	120	130	130	125	120	120	120
10	75	110	115	125	135	140	145	150	145	140	135
14	70	90	100	115	125	125	120	120	115	115	110

To test our assumption that a variation in the proportion of water in the dough would be reflected in the power required to mix doughs, a series of doughs made with a spring wheat patent flour was prepared with proportions of water ranging from 57% to 71% by increments of 2%. The average power requirement in watts at the end of 6 minutes of mixing of each of these doughs is recorded in Table II. It will be observed that the decrease in power requirement was fairly regular in progressing from 57% to 67% of water, but thereafter each unit increase in water resulted in a small decrease in the power requirement.

TABLE II

EFFECT OF VARYING AMOUNTS OF WATER ON POWER REQUIRED TO MIX DOUGH (SPRING WHEAT PATENT FLOUR)

Water %	57	59	61	63	65	67	69	71
Av. power after 6 minutes, watts	185	170	160	142	125	108	104	102

Another series of doughs was then prepared to which was added 6 grams of dry skimmilk for each 100 grams of flour in the dough. It was evident at once that the quantity of water required was substantially increased and accordingly the first dough was prepared with

67 cc. of water for each 100 grams of flour. Four additional doughs were mixed with increasing proportions of water in increments of 2 cc. for each 100 grams of flour. On comparing the resulting measurements of power requirement, recorded in Table III, with similar data obtained with the milk-free doughs, recorded in Table II, it appeared that in general one cc. of water was required for each gram of dry skimmilk superimposed upon the control dough formula.

TABLE III

EFFECT OF 6% OF DRY SKIMMILK UPON THE POWER REQUIRED TO MIX THE DOUGH

Water %	67	69	71	73	75
Av. power, after 6 minutes, watts	168	143	135	110	60

This assumption was confirmed by the further observation that control doughs prepared with 65 cc. of water per 100 grams of flour were seemingly of the optimum consistency, while the dry skimmilk doughs prepared with 71 cc. of water for each 100 grams of flour likewise were of the optimum consistency in the second or milk series.

Previous to undertaking these experiments it had been stated in the trade press that dry skimmilk should be reconstituted with water before being used in bread making. Accompanying these suggestions was the intimation that in this wise the maximum absorption of water by the milk dough can be effected. To test this suggestion an extended series of experiments was next conducted in which the length of time that the reconstituted milk was allowed to stand after the addition of water was the variable. In all these trials the equivalent of 6 grams of dry skimmilk was used with each 100 grams of flour in the dough batch. The interval of time that the reconstituted milk was allowed to stand ranged from 2 hours to 14 hours. This reconstituted milk was the sole liquid added to the dough. The power requirement of the mixing unit (after deducting the power requirement of the empty machine) was noted at regular intervals of time up to 18 minutes. The resulting observations are recorded in Table I. Any advantage in allowing the reconstituted milk to stand for more than 2 hours is not apparent from these observations. While the power requirement in terms of watts does not progress regularly, either with the time of mixing or with the length of time that the reconstituted milk stood, the results are probably as regular as might be anticipated without including many replicates. In a general way the milk that was reconstituted 2 hours before mixing the dough was as effective in increasing the absorption of the dough as the milk which stood for materially longer periods of time.

Studies of Absorption with the Chopin Extensimeter

A Chopin extensimeter was made available through the courtesy of the Washburn-Crosby Company and a series of observations was made involving a measurement of the force required to extend a dough surface. The device was described by Chopin (1921) and by Bailey and Le Vesconte (1924). A recording pressure gauge has been attached to the device since Bailey and Le Vesconte reported their experiments.

In using this device simple doughs were mixed, using flour and 2.5% sodium chloride solution. Proportion of water to flour and proportion of dry skimmilk to flour were the only variables. When pressure was applied to one face of a sheet of dough three millimeters thick, the area of the surface could be extended, and the pressures required to effect this extension were traced by the stylus of the recording pressure gauge. These pressures tended to rise to a rather definite maximum and then receded with a further extension of the surface until the latter ruptured, when the pressure immediately receded to zero.

With the proportion of water as a variable, the maximum pressure thus recorded tended to diminish as the quantity of water was increased. In the experience of this laboratory, pressures equivalent to 90+ mm. (of water) were usually encountered in doughs that were deemed to be of the optimum consistency. When dry skimmilk was superimposed upon the simple formula there was an apparent tendency toward an increased pressure, altho the results were not as clean cut and definite as were secured through the use of the watt meter. This is evident from the data recorded in Table IV.

TABLE IV

PRESSURE IN MM. OF WATER, OR FORCE REQUIRED TO EFFECT EXTENSION OF DOUGH, MEASURED WITH THE CHOPIN EXTENSIMETER

Water, cc. per 100 grams flour	Dry skimmilk, %		
	0	5	10
63.0	135		
65.7	....	....	120
68.6	75	70	90
71.4	50	60	
77.1	40	50	
80.0	....	....	50

The Chopin device also provided means for measuring the extension of surface of dough that can be effected before the thin film of dough bursts. This is termed by Chopin "the coefficient of extension" and is recorded directly from the graduated gasometer which is provided with the instrument. This coefficient of extension was measured in a series of doughs prepared with varying ratios of water

to flour and of dry skimmilk to flour. A summary of the replicated measurements expressed as the mean of the replicates and the probable error of this mean appear in Table V. In each of the series with the proportion of water to flour as a variable it appeared that the coefficient of extension tended to pass through a maximum as the proportion of water was increased. This maximum was of about the same order in each of the series of doughs, indicating that proportions of dry skimmilk as high as 10 grams per 100 grams of flour did not have a large effect upon this property of the dough. The interpretation of these measurements of "coefficient of extension" in terms of baking qualities of the dough cannot yet be made as effectively as is desirable.

TABLE V

COEFFICIENT OF EXTENSION OF DOUGHS MADE WITH VARYING PROPORTIONS OF WATER AND OF DRY SKIMMILK AS MEASURED WITH THE CHOPIN EXTENSIMETER

Water, cc. per 100 grams of flour	Coefficient of extension (Mean of replicates and probable error of mean) Milk per 100 g. flour				
	0.0g.	2.5g.	5.0g.	7.5g.	10.0g.
63.0	19.1±0.33	.....	.....	.....	.....
65.7	.....	17.5±0.24	.....	16.8±0.33	16.7±0.22
68.6	21.7±0.27	21.9±0.39	23.0±0.62	.....	17.9±0.62
71.4	21.3±0.39	23.9±0.47	23.9±0.37	22.5±0.35	.....
74.2	.....	.....	.....	23.6±0.46	22.8±0.43
77.1	22.7±0.82	.....	24.5±0.74	21.8±0.48	.....
80.0	.....	.....	.....	.....	19.3±0.45
82.9	.....	.....	15.8±0.80	.....	.....

Plasticity of Flour-in-Water Suspensions Containing Dry Skimmilk

Bingham and Murray (1923) proposed a form of plastometer that proved convenient in securing a series of measurements upon a preparation. The form of plastometer used in this study involved the use of a capillary tube having a reasonably uniform bore, and carefully calibrated for each 10-cm. section. This capillary tube was firmly sealed into the end of a heavy metal reservoir. The reservoir was so constructed that it could be filled with the material under observation and then sealed tightly except for the tubulure through which pressure was applied. The tubulure was connected by means of pressure tubing to a steel tank having a capacity of about 140 liters. The air pressure in the tank was raised by means of a hand pump and was registered on a simple water manometer. The plastometer, supported on a special frame, could be completely immersed in a water thermostat so designed as to permit control within less than ±0.1° C.

The calibration of the capillary tube was effected by first dividing the tube into 10-cm. sections, measuring from the inlet end. A quantity of mercury was then introduced that would fill the bore of the tube for approximately 10 cm. The actual length of the mercury column in

each of the 10-cm. sections was then measured with vernier calipers. The mercury was then removed from the tube and weighed.

Typical calibrations, which resulted from the observations in tube 1, appear in Table VI. The volume of each 10-cm. section of the bore of the tube was computed and this constitutes the Δv which appears in the formula developed by Kelly (1925). The time required for the material under observation to flow through each 10-cm. section could then be measured with a stop watch and the resulting observations constituted the Δt of the same formula. From these two formulas the rate of flow $\Delta v / \Delta t$ was calculated and plotted against the shearing stress for the respective sections of the tube.

TABLE VI

CALCULATION OF CONSTANTS FOR TUBE 1. WEIGHT OF MERCURY = 6.7522 G. VOLUME = .49854 CC

	Length of mercury column in each section cm.	Radius cm.	Volume cc.	Average radius	r^4	$\frac{l_2+l_1}{2}$	$\frac{\eta r^4 \times 980}{8\left(\frac{l_2+l_1}{2}\right)}$
1	10.03	0.12575	0.49705	0.12575	0.00025005	5	
2	10.03	.12575	.49705	.12575	.00025005	15	
3	10.10	.12530	.49360	.12560	.00024886	25	
4	10.14	.12510	.49176	.12547	.00024783	35	0.002725
5	10.14	.12510	.49176	.12540	.00024728	45	.002115
6	10.02	.12580	.49755	.12547	.00024783	55	.001735
7	10.04	.12570	.49656	.12550	0.00024807	65	0.001469
8	10.06	0.12560	0.49556	0.12551			

The shearing stress was calculated from the formula of Kelly $\frac{\eta r^4 g p}{8\left(\frac{l_2+l_1}{2}\right)}$ in which

r = average radius between l_2 and l_1

g = gravitational constant (taken as 980 dynes)

p = pressure in cm. of water

l_2, l_1 are distances from entrance of capillary between which the readings were taken.

This formula involved the assumption that the radius of the tube is uniform between the points l_1 and l_2, which is not necessarily the case. Such small errors as are introduced with this assumption are less than the experimental error of timing the flow.

With flour suspensions it was found desirable to consider the zero time as the instant when the advancing column of fluid passed the graduation 30 cm. from the inlet end of the capillary. The rate of flow was then measured through the next four succeeding intervals of 10 cm. each. As two constants, η and g appear in the numerator of

the shearing stress formula, it became possible to introduce the proper values for r^4, and the intervals represented by the values l_2 and l_1 into the formula as it fits each of these four 10-cm. intervals. The appropriate values for tube 1 were thus computed and are recorded in the right hand column of Table VI. Multiplying these values by the pressure applied, as registered on the manometer, gave the shearing stress in dynes per square cm. for these four sections of the tube. These pressures were commonly held between 40 cm. and 41 cm. and the observations reported in this table were all made with the thermostat maintained at 25° C.

A typical series of observations is recorded in Table VII. If the values for rate of flow $\Delta v / \Delta t$, were used as one set of co-ordinates (y) and the shearing stress values as the other set of co-ordinates, (x), the resulting plot approached a straight line. The slope of this line, or the tangent that it formed with the horizontal axis, afforded a graphic measure of mobility. As experimental errors not infrequently resulted in slight deviations from a straight line when the data were plotted, it proved convenient to compute the tangent of the angle by the method of least squares, using the formula: $b = \frac{\Sigma(x)\Sigma(y) - n\,\Sigma(xy)}{[\Sigma(x)]^2 - n\,\Sigma(x^2)}$. By extrapolation of the straight line curve representing the relation of rate of flow to shearing stress to its intersection with the x axis (shearing stress), the yield value could likewise be computed.

TABLE VII

CALCULATION OF THE MOBILITY OF A FLOUR-WATER SUSPENSION
Pressure (cm. water) 40.8

Observed time min.	Δt	$\frac{\Delta v}{\Delta t}$	$\frac{\eta r^4 \times 980 \times P}{8\left(\frac{l_2+l_1}{2}\right)}$
4.2			
10.0	5.8	0.084786	0.11118
18.2	8.2	.059970	.08629
29.8	11.6	.042892	.07079
44.0	14.2	0.034960	0.05994

Mobility, calculated by method of least squares = 0.991

In a series of preliminary observations upon flour suspensions it appeared that preparations consisting of 30 grams of flour suspended in 70 cc. of water were most suitable for plasticity measurements. With more concentrated preparations the capillary tube tended to plug and it was very difficult to clean it for the next determination. With less than 30 grams of flour to 70 cc. of water the rate of flow through the tube selected for this work was too rapid to permit accurate timing. In preparing the flour suspensions, the mixture of flour and water was

triturated very lightly in a mortar, care being taken to avoid a grinding action.

In the preliminary work it also became apparent that the time these preparations stood before observations were made upon them must be accurately standardized. This is evident from the observations reported in Table VIII, where the time of standing, in minutes, was the variable and the mobility as computed in the manner indicated has been recorded in the instance of replicated determinations. It appeared that mobility of the preparation increased with the lapse of time.

TABLE VIII

MOBILITY OF SUSPENSIONS CONTAINING 30 GRAMS OF FLOUR AND 70 CC. OF WATER

Time of standing, min.	Mobility						
							Average
30	0.94	0.91	1.04	1.09	1.21	1.11	1.05
60	1.06	1.06	1.26	1.08	1.16	1.05	1.11
90	1.24	1.56	1.18	1.45	1.28	1.22	1.32
120	1.42	.....	1.45	1.38	1.31	1.30	1.37
150	.....	.....	1.56	.....			
320	.....	.....	.....	1.88			
490	.....	.....	.....	1.98			

A second series of observations was then made in which 1.8 grams of dry skimmilk was superimposed upon the flour-water mixture, consisting of 30 grams of flour and 70 cc. of water. The preparations were allowed to stand for varying lengths of time and the mobility of the resulting suspensions is recorded in Table IX. When the data in Table IX were compared with those in Table VIII it appeared that the addition of the dry skimmilk has effected a decrease in the mobility of the preparation. Moreover, a reduced rate of change in mobility with the lapse of time was evident when the milk was present, particularly between the 60th and the 120th minute. This indicated that the dry skimmilk constituents either held the imbibed water for a longer time, or tended to imbibe the water more slowly so that the imbibitional period is longer. In other words, the dry skimmilk seemingly increased the stability of the system.

TABLE IX

MOBILITY OF SUSPENSIONS CONTAINING 30 GRAMS OF FLOUR, 1.8 GRAMS OF DRY MILK, AND 70 CC. OF WATER

Time of standing, min.	Mobility					
						Average
30	0.91	0.99	0.98	0.95	0.90	0.95
60	0.88	1.20	1.13	1.20	1.03	1.09
90	0.95		1.07	1.38	1.10	1.12
120	1.16		1.24	1.17	1.06	1.16

To indicate the direct effect of dry skimmilk upon the mobility of flour suspensions, a series of measurements was made in which the ratio of flour to water was maintained at a constant level (30:70) in the controls, while the proportion of water was progressively increased in like preparations upon which 1.8 parts of dry skimmilk had been superimposed. The resulting data are recorded in Table X. With the same proportion of water, the mobility of the suspension was reduced when milk was added. As nearly as can be computed from these data, somewhat less than 2 cc. of water was required to compensate for the 1.8 grains of added dry skimmilk, using the values for mobility at the 90th and 120th minutes. This tends to confirm the estimates based upon power-input readings with the wattmeter and dough-mixing machine—that approximately one unit of water by weight was required to compensate for each unit of added milk in adjusting flour-water-milk mixtures to the same degree of plasticity.

TABLE X

MOBILITY OF SUSPENSIONS CONTAINING 30 GRAMS OF FLOUR WITH AND WITHOUT 1.8 GRAMS OF DRY SKIMMILK WITH VARYING AMOUNTS OF WATER (AVERAGE VALUES)

Time of standing, min.	Control 30 gm. flour	Control with Dry Skimmilk				
		cc. of water				
	70	70	71	72	73	74
30	1.05	0.95	1.00	1.12	1.15	1.20
60	1.11	1.09	1.13	1.20	1.30	1.32
90	1.32	1.13	1.20	1.37	1.31	1.47
120	1.37	1.16	1.19	1.40	1.43	1.53

A study was also made of the relative mobility of solutions of dry skimmilk alone. A mixture of 40 grams of the milk and 60 cc. of water had about the same mobility as the suspension of 30 grams of flour and 70 cc. of water. This suggests the conclusion that the dry skimmilk has a lower water-imbibing capacity than flour. Even tho this be true, mixtures of the two components require more water to bring them to a definite plastic state than is indicated by observations upon the separate components, indicating that such mixtures have a larger "absorption" than either the dry skimmilk or the flour alone.

Summary

Power required to operate a dough-mixing unit tends to decrease as the proportion of water present is increased.

Dry skimmilk increases the water-imbibing capacity of dough as indicated by the power-input. It proved necessary to add about one unit of water by weight for each unit of dry skimmilk to maintain the same degree of plasticity in the dough as measured with the wattmeter and motor-driven mechanical dough mixer.

Force required to extend dough surface, as measured with the Chopin extensimeter likewise tended to decrease as the proportion of water was increased. This was observed both with the control or milk-free doughs and with those containing dry skimmilk.

Extensibility of doughs, as measured with the extensimeter, was not substantially affected by the inclusion of 10% or less of dry skimmilk in the dought.

Plasticity of flour-water, and flour-water-dry skimmilk suspensions was measured by Bingham and Murray's method. The mobility of such suspensions increased with time through several hours.

Mobility of such suspensions decreased with the additions of dry skimmilk. About one unit by weight of additional water was required with each unit of dry skimmilk to maintain the same relative mobility when the milk was added to flour-water suspensions.

Literature Cited

Bailey, C. H., and Le Vesconte, Amy M.
1924 Physical tests of flour quality with the Chopin extensimeter. Cereal Chem. 1:38-63.

Bingham, E. C. and Murray, H. A.
1923 A new combined viscometer and plastometer. Proc. Am. Soc. Test Materials 23:655.

Briggs, C. H.
1918 Briggs' perfekdo viscometer. Northwestern Miller, 113:275.

Chopin, Marcel
1921 Relations entre les proprieties mechaniques des pates de farines et la panification. Bul. soc. encour. ind. nat. 133:261-273.

Harrel, C. G.
1927 A gravimetric penetrometer for measuring stiffness or toughness of doughs. Cereal Chem. 4:283-290.

Jago, W. and Jago, W. C.
1911 The technology of bread-making. London.

Kelly, W. J.
1925 The plasticity of rubber and its sols. Colloid Symposium Monograph 3: 303. Chemical Catalog Co. New York.

Mangels, C. E.
1928 Relation of water absorbing capacity of flour to protein content, baking quality, and loaf weight. Cereal Chem. 5:75-77.

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